VOL. XIV. [JANUARY, 1892.] No. 1.

AMERICAN

CHEMICAL JOURNAL.

ON THE ISOMORPHISM AND COMPOSITION OF THORIUM AND URANOUS SULPHATES.

BY W. F. HILLEBRAND AND W. H. MELVILLE.

I.—CHEMICAL DISCUSSION.

BY W. F. HILLEBRAND.

During the course of an extended investigation on uraninite[1] it was often necessary to decompose the mineral in sealed tubes with sulphuric acid. At first a deposit was generally observed on removing the tubes from the oven, the character of which depended on the concentration of the acid and the presence or absence of thoria in the mineral. In the absence of this earth it took the form of a greenish powder with a strong acid, and of bright green, brilliantly reflecting crystals when a weak acid was used, unless the ratio of liquid to mineral was sufficiently high in the latter case to prevent crystallisation. As might naturally be supposed, these crystals were hydrated uranous sulphate. The best results as regards size of crystals were obtained with an acid containing one part of sulphuric acid to five or six of water by volume. With about 100 parts by weight of such an acid to one of the oxide UO_2, it might pretty confidently be expected that no crystallisation would take place.

In presence of thoria the green crystals still appeared, but they then contained thorium as well as uranium, and accompanying them was a beautiful, white, coherent, spongy mass, extending the length of the tube and consisting of a network of microscopic

[1] Bull. U. S. Geol. Survey, **78**, 43, 1889-1890.

needles grouped in radiating bunches. This was likewise a double sulphate of uranium and thorium, resembling in every respect the deposit formed under similar conditions from a solution of thorium sulphate alone, except that when washed, dried, and compacted together there was a faint greenish tinge to it. Ordinarily the two forms of double salt appeared together, and it even seemed as if under favorable conditions, which have not yet been precisely determined, the crop of green crystals might be increased at the expense of the white deposit. At least on one occasion, when the heating was prolonged for several days, the latter gradually disappeared while the former increased in size and number. The white deposit always preceded the green crystals, and by regulation of the proportions of oxide and of acid, and of duration of heating, it is possible in practice to obtain the former alone, if desired.

In order to secure material for exact chemical and crystallographical determinations, recourse was had to the artificially prepared oxides U_3O_8 and ThO_2, by using which, either alone or mixed in varying proportions, different products were obtained. Neither uraninite nor uranium dioxide, UO_2, is well adapted for this purpose, because of contamination of the crystals by sulphate of lead in the one case and by undissolved dioxide in the other. Even when using the oxide U_3O_8, care must be taken to avoid a like result, by fine pulverisation and avoidance of excess of oxide as compared with acid. So slightly soluble are the green crystals that over 50 per cent. of the dioxide UO_2 in uraninite, or in the oxide U_3O_8, can generally be obtained as sulphate. Hence it follows that when the dioxide is to be estimated volumetrically, care must be taken to use sufficient dilute acid to render impossible the formation of these crystals. The white, spongy deposit is not a hindrance to the exact estimation of the dioxide by potassium permanganate, for it dissolves readily in cold water, though with extreme slowness when once it has been compressed.

The green crystals were separated from their mother-liquor in a Gooch crucible, without asbestus felt, with the aid of suction; they were at once washed with hot dilute sulphuric acid, then with alcohol, and finally with ether. They were allowed to dry thoroughly in the air and were analysed in that condition. It was found by experiment that alcohol was practically without solvent action on the sulphates, and that none of the water of crystallisation

was removed by it. If both forms of deposition occurred at one time, the spongy one was first removed with great ease by two or three rapid washings with cold water—the network of fine needles being partly dissolved and partly carried through the holes in the crucible by the powerful suction—after which alcohol and ether were used as before. The results of analyses were as follows:

	I.	Molecular ratio.	II.	Molecular ratio.
UO_3	49.18	1.00	48.40	1.00
ThO_2	3.59	...	5.58	...
SO_3	32.08	2.05	31.27	1.96
H_2O	14.18	4.04	14.84	4.13
	99.03		100.09	

A sample of uraninite decomposed by dilute sulphuric acid in a tube at about 170° C. furnished the product whose analysis is given under I. An earlier and very similar analysis of another preparation may be found on p. 50 of the bulletin cited. The loss is mainly, if not altogether, undetermined lead oxide from included lead sulphate, which accounts in part for the excess of SO_3 found. For No. II the oxides U_3O_8, ThO_2 were taken in such proportion that there should be about six times as much uranium dioxide as of thorium dioxide. Inasmuch as only 0.1622 gram was available for sulphuric-acid and water determinations in this analysis the ratio is not bad. One or two attempts to obtain a product with more thorium and less uranium by starting with correspondingly different proportions of the oxides ThO_2 and U_3O_8, were unsuccessful, perhaps because of the tendency of thorium sulphate to separate at once in the spongy state and thus to reduce the amount available for slow crystallisation with the uranium. The specific gravity of No. II was kindly determined by Mr. L. G. Eakins in alcohol of 0.7956 density. It was found to be 4.563 at 24.3° C., which, calculated for water at the same temperature as standard, becomes 3.63. The material examined contained 1.04 per cent. of the oxide U_3O_8 undissolved, which does not appear in the analysis, and, allowing for this a density of 7.3 (Clarke's Tables), that of the double sulphate having the given composition is found to be 3.61 at 24.3° C.

The uranium sulphate, of which the analysis is here given, was obtained by decomposing the oxide U_3O_8 with dilute sulphuric acid in the manner already mentioned. Its density was not ascertained.

	III.	Molecular ratio.
UO_3	53.99	1.00
SO_3	31.94	2.00
H_2O	14.13	3.94
	100.06	

It appears, as was to be expected, that thorium is capable of replacing uranium in the sulphate of the latter which holds in combination four molecules of water. That this is a true case of isomorphism is most fully shown by Mr. W. H. Melville in the crystallographical part of this paper, although the habit of the uranium sulphate differs from that of the double salt.

While, as above stated, failure resulted from attempts to lower the ratio between thorium dioxide and uranium dioxide in the green double salt, it was found that the spongy mass, which almost always formed in the tubes when thoriferous uraninite was decomposed with dilute sulphuric acid, contained a very much higher proportion of thorium, and that by taking the dioxides in varying proportions, double salts of correspondingly different composition could readily be obtained, as is shown by the following analyses:

	I.	Molecular ratio.	II.	Molecular ratio.
UO_3	34.34	1.00	16.92	1.00
ThO_2	19.84		36.07	
SO_3	31.48	1.95	32.66	2.05
H_2O(diff.)	14.34	3.95	14.35	4.01
	100.00		100.00	

Both salts were obtained from a mixture of the oxides U_3O_8 and ThO_2. In the case of No. II, the proportion was such that the uranium dioxide of the compound U_3O_8 was to the oxide ThO_2 as 2 to 1. It happened that the tube containing this preparation lay unopened for several weeks after removal from the oven, but during this time there had been no perceptible resolution of the precipitate, which on agitation made a thick emulsion with the acid. Both products were thrown on a Gooch crucible without asbestus felt, quickly washed twice or thrice with hot dilute sulphuric acid, and then with alcohol and ether, whereupon they were allowed to dry thoroughly in the air.

There is no reason to doubt the isomorphism of this salt with that formed under similar conditions from thorium alone, but whether these are crystallographically referable to the green crys-

tals before described, or form a new case of dimorphism, must remain undetermined until the crystallographic features of the former are known. In polarised light, the needles of the double salt extinguish apparently parallel to their length.

Such contradictory statements appear in the literature of the subject regarding the composition of thorium sulphate separated from hot acid solutions—some authorities claiming $4\frac{1}{2}$ molecules of water of crystallisation and others only 4—that it is very satisfactory to have evidence like that furnished by the above analyses to throw light upon the question. The tendency of late years has been to admit a mutual replaceability of thorium dioxide and uranium dioxide in chemical compounds, though no direct proof seems to have been heretofore established, and it was therefore reasonable to suppose that the composition of the thorium sulphate in question should correspond with that of the well-known uranous sulphate with 4 molecules of water. In the light of the above analyses there is no room to doubt the complete isomorphism of the two sulphates, and that Demarcay[1] and Roozeboom[2] were right in accepting the formula $ThO_4(SO_3)_2.4H_2O$, derivable from the more or less incomplete analyses of Berzelius, Berlin, and Chydenius, in preference to $ThO_4(SO_3)_2.4\frac{1}{2}H_2O$, afforded by the more numerous ones of Delafontaine.[3]

In possible explanation of Delafontaine's high results for water, Roozeboom[4] very justly remarks that because of its physical character the salt retains much mother-liquor, and that if this be not removed at a temperature above 45° C., the $9H_2O$ salt is formed from it on cooling, so that it is almost impossible not to find too much water. Notwithstanding numerous attempts to prepare the salt $ThO_4(SO_3)_2.4H_2O$ from hot acid solutions as well as from warm neutral ones, I have never myself succeeded in reducing the water to four molecules, even though the mass of needles was rapidly washed with hot dilute sulphuric acid and then with alcohol and ether, after freeing from mother-liquor by power-

[1] Compt. rend. **96**, 1860.

[2] Ztschr. phys. Chem. **5**, 198.

[3] Ann. Chem. (Liebig) **131**, 100. The statement by Kraut, near the foot of page 687 of Gmelin-Kraut's Inorganic Chemistry, Vol. II, Part I, is manifestly unwarranted. He considers the evidence in favor of the $4H_2O$ salt as insufficient, and thinks the analyses affording this formula were made upon mixtures which might have resulted through absorption of water by the $3H_2O$ salt. It is strange that individuality should have been accorded by Chydenius and Cleve to this latter salt, which the former obtained by drying over sulphuric acid, after washing with hot water, the precipitate formed by boiling a weakly acid solution of the sulphate. Roozeboom is certainly correct in excluding this $3H_2O$ salt from the list of thorium sulphates.

[4] Loc. cit., p. 202.

ful suction on a Gooch crucible without asbestus felt, but my faith in the correctness of the formula with $4H_2O$ is not hereby shaken. A further possible cause of high results will appear from the following: The air-dried salt is said by Delafontaine to be thoroughly non-hygroscopic, and for a given temperature and hygrometric condition of the atmosphere it is true that no change in weight does occur; but if the salt be weighed from day to day, or even twice a day, a very marked gain or loss of weight is observed, depending in degree on the amount of change in the atmospheric conditions. In August and September, when hygrometric and thermometric readings were often high, and marked and rapid changes were not infrequent, this gain or loss sometimes amounted within 24 hours to over 0.5 per cent. of the total weight of the salt, and the extreme change during those months reached 1.22 per cent. It is therefore patent that the formula afforded by analysis may materially depend on whether the salt analysed was weighed when the weather was hot and moist or cold and dry.

It may not be out of place here to call attention to a possible cause of the frequent discrepancies noticed in the statements of different writers in regard to the amounts of water given off by different substances when placed over sulphuric acid in a desiccator. No one would deny that sulphuric acid of maximum concentration is superior as a drying agent to the same acid somewhat, if only slightly, diluted; but it is probably not known to every one how much may depend on the strength of the acid used. A case in point is the following: A thorium sulphate containing, air-dried, 15.22 per cent. H_2O, or 4.23 molecules, lost weight over concentrated sulphuric acid in a tightly closed desiccator as shown in column I, and as in column II over acid which had been in use in another desiccator for a considerable length of time and was subsequently found to have a density of 1.66. The cases are not rigidly comparable perhaps because of the different times devoted to the experiments, which were not carried on simultaneously, but they serve to illustrate the point.

Time in days.	I. Acid of 1.84 sp. g.	Time in days.	II. Acid of 1.66 sp. g.
1	3.80 per cent.	1	2.87 per cent.
3	2.78	1	.40
5	1.37	3	.06
9	0.22		
18	8.17	5	3.33

This may be considered an extreme case, but it shows plainly the importance of using fresh acid of full strength whenever experiments of this kind are to be made, in order that results may be properly comparable.

Similarly it is improbable that a highly hydrated substance, which loses much of its water at 100° C., would show as great a loss when dried in an ordinary air-bath as in a current of dry air of that temperature.

Another point to be considered when it is desired to find the maximum amount of water that can be removed by any drying agent in a desiccator (which of course as a method is in general inferior to that in which a continuous current of dry air or other gas is passed over the substance) is that, if many days are required for its removal—in other words, if the substance is slow to part with its moisture—the later weighings should not be made from day to day but at ever increasing intervals, otherwise a prematurely constant weight or even an increase may be observed. This is due to the fact that whenever the desiccator is opened, which must be twice for each weighing, it, at least in the upper part, becomes filled with moist air, and the substance itself may absorb some moisture before it can be returned to the desiccator; one or more days may then be required to restore the condition of equilibrium which obtained between the vapor tensions of water in the salt and in the air of the desiccator prior to opening the latter. Especially if the acid has become somewhat weakened is it possible for an increase to take place.

Originality is not claimed for the above observations on methods of drying, but it seems as if attention could not be too strongly or too frequently drawn to the points mentioned, which there is reason to fear are not always observed.

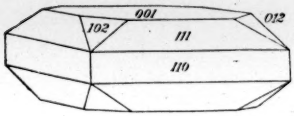
II.—Crystallographical Discussion.

By W. H. Melville.

The green crystals of sulphate of uranium and of the double sulphate of uranium and thorium described by Mr. Hillebrand are isomorphous and their crystallographic elements are almost identical. The angles between corresponding faces of the two salts differ by less than 1°, while their axial ratios are the same up to the second decimal place. Indeed, the axes plotted for the drawing of the crystals of one salt served for the drawing of those of the other.

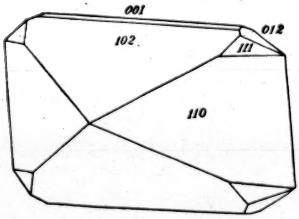
URANIUM SULPHATE.

1.



URANIUM-THORIUM SULPHATE.

2.



The two sulphates crystallise in the prismatic (orthorhombic) system. The habits of the two sets of crystals are quite unlike, and by simple inspection no analogy would seem to exist between them, since those of the double sulphate of uranium and thorium have all the appearance of the pyramidal (tetragonal) combination of forms.

On the goniometer the simple sulphate of uranium presented the most perfect faces, so that very accurate measurements were obtained. On the other hand the similar angles of the double sulphate showed great variations in the readings, often amounting to a difference of 40′ from the mean value. The difficulty of preserving in artificial crystals the same brilliancy of faces, after drying, which they possess in the mother-liquor, accounts for the broad bands of these reflect signals. However, after its system of crystallisation was identified, the mean of the most perfect and reliable measurements was taken.

The crystals of the double sulphate of uranium and thorium were often twinned, the twinning plane being parallel to (100). Also individuals occurred on the faces (102) and ($10\bar{2}$) which were composed of the face (110) in combination with minute planes of the forms (111) and (012).

The forms observed on the crystals of both salts were the same, but unequally developed, as the accompanying figures illustrate, in which the degree of development in the originals has been preserved. Forms: {001}, {010}—always a very narrow plane which does not appear in the drawings—{110}, {111}, {102}, {012}. Measurements:

(1) Uranium Sulphate.	Measured.	Calculated.
001 ∧ 111	70° 57′	70° 56′ 30″
001 ∧ 102	52° 13′	52° 10′ 7″
001 ∧ 012	33° 49′	33° 28′ 14″
111 ∧ 1$\bar{1}$1	51° 9′	} fundamental.
111 ∧ 110	19° 3′ 30″	
110 ∧ 1$\bar{1}$0	54° 23′	54° 21′
102 ∧ 10$\bar{2}$	75° 34′	75° 39′ 46″

Axial ratio: $\breve{a} : \bar{b} : \dot{c} = 1 : 1.9478 : 2.5755$.

(2) Double Sulphate of Uranium and Thorium.	Measured.	Calculated.
001 ∧ 102	51° 57′	51° 57′ 37″
001 ∧ 012	33° 25′	33° 39′ 38″
111 ∧ 1$\bar{1}$1	51° 46′	} fundamental.
111 ∧ 110	19° 8′	
110 ∧ 1$\bar{1}$0	55° 14′	55° 2′ 24″
102 ∧ 10$\bar{2}$	76° 6′	76° 4′ 46″

Axial ratio: $\breve{a} : b : \dot{c} = 1 : 1.9194 : 2.5563$.

LABORATORY OF THE U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C., *Nov.* 1891.

Contributions from the Chemical Laboratory of Purdue University.

VI.—THE DIGESTIBILITY OF THE PENTOSE CARBOHYDRATES.

BY W. E. STONE.

In some previous papers, attention has been called to the occurrence and properties of a class of bodies for which the names *pentosans* or *pentose carbohydrates* have been proposed.[1] It has

[1] This Journal **12**, 435; **13**, 73 and 348. Ber. d. chem. Ges. **21**, 1572 and 2148; **23**, 2574 and 2791; **24**, 1657 and 3019. Ann Chem. (Liebig) **249**, 227 and 257. J. Anal. and Appl. Chem. **5**, 421. Agric. Sci. **2**, 315; **5**, 91.

been shown that they occur more or less abundantly in most plant tissues, and hence in many food materials; that they are soluble in dilute alkalies; that they are converted into sugar-like bodies by the action of dilute acids, and that these sugars (the pentoses) respond to many of the reactions for the true sugars or glucoses. In short, by the ordinary analytical operations they may easily elude recognition when accompanying the true carbohydrates. From this it is clear that a food analysis, in which the "crude fibre," "crude protein," and "nitrogen free extract" have been determined by the ordinary methods, does not distinguish between these pentosans and such true carbohydrates as starch, sugar, etc. It is indeed possible, by the standard methods, to obtain apparently a large percentage of starch from materials which contain no starch whatever, the result being due to the presence of pentosans and the pentoses derived from them. But while these bodies are thus indiscriminately classified with others of quite different nature, so far as analytical results go, we are not justified in assuming that they possess equal nutritive value or digestibility. Indeed, in a general way, a low nutritive value has been ascribed to them, although there were few experimental facts to support such an assumption. Some twenty years ago, Gudkow recognised the presence of a body in wheat bran, which upon inversion yielded a sugar which was not glucose. In order to isolate it from the starch of the bran, he caused the latter to be fed to swine, and found that the unknown body actually resisted the digestive action to which the true carbohydrate succumbed.[1] He was unable to identify the body, but it has since been shown to be a pentosan from which arabinose may be derived.[2]

While recognising the existence of such bodies in vegetable food materials, it has hitherto been impossible to study their digestibility or physiological role experimentally, because of the lack of any analytical process by which they could be estimated separately from the other carbohydrates. Hence digestion experiments have exhibited this fallacy, viz., that while a homogeneity of composition and a constant value were assumed for the "nitrogen-free extract," it has been well known that it included a number of bodies of quite variable nature. This also holds true of the class of nitrogenous bodies classified as "crude protein," which

[1] Ztschr. Chem. [2] **6**, 360.
[2] Ann. Chem. (Liebig) **249**, 239; also Ber. d. chem. Ges. **23**, 3110.

are known to have a widely varying character and value, so far unrecognised in analytical methods save in a general division into albuminoids and non-albuminoids.[1]

Within a few years, however, specific qualitative reactions for the pentosans have been discovered, and one of these has of late been developed into a quantitative method of reasonable accuracy.[2] By this method it is possible to estimate the pentosans quite independently of the presence of accompanying carbohydrates, by converting them into furfurol, and titrating the latter with a solution of phenyl-hydrazine of known value. This, for the first time, renders possible the estimation of these bodies under all conditions, and allows analytical control of experiments as to their digestibility. Such an experiment has for the first time been carried out in this laboratory, and although simple in its details, the results seem worthy of record.

Rabbits were supplied with natural food containing appreciable quantities of pentosans, the amount and composition of both the food consumed and dung excreted being controlled by analysis. All of the ordinary rules controlling such experimentation were carefully observed. The experiment covered two periods, separated by a proper interval. The food selected for the first period consisted of a mixture of equal weights of wheat bran and cornmeal, the whole making a fairly normal sustenance ration. During the second period the food consisted of wheat bran alone. In both periods the bran supplied the desired pentosans, of which it contained sufficient quantities to produce 7.16 per cent. of furfurol. The two rabbits employed were fed with the specified food during six or eight days previous to the beginning of the periods in which the data were collected. During the feeding periods, all the food consumed was carefully weighed, and all the dung collected. The latter was afterwards weighed in an air-dry condition, corresponding to the state of the food. Finally, all of the materials were subjected to the ordinary fodder analysis, in addition to which the pentosans in all were determined by the method already cited.

[1] Prof. Tollens has lately published in Die landwirthschaftlichen Versuchs-Stationen 39, 401, an interesting resumé of the researches of himself and pupils, showing the varied character of these constituents of the "nitrogen-free extract," with their characteristic reactions. In closing he says: "In any case the old-style determination of the 'nitrogen-free extract,' however convenient and useful it may have been, requires modification at the present time."

[2] J. Anal. and Appl. Chem. 5, 421.

The first period lasted ten days, and the food employed was the mixture of bran and meal. "Hans" consumed 533.8 grams and voided 118 grams of dung. "Max" consumed 344.0 grams and voided 71.8 grams of dung.

Analyses of the materials gave the following results:

	Food. Per cent.	Dung of Hans. Per cent.	Dung of Max. Per cent.
Moisture,	11.71	10.93	10.42
Ash,	3.71	9.45	9.92
Fibre,	5.42	16.48	19.43
Protein,	12.69	18.63	17.00
Ether extract,	4.03	2.07	1.64
N-free extract,	62.44	42.44	41.59
Furfurol obtained,	4.64	8.62	8.30
Pentosans (= furfurol × 1.38),	6.40	11.90	11.45
Proportion of pentosans in N-free extract,	10.25	28.04	27.53

The furfurol obtained stands for a certain amount of pentosans in the materials, but in just what proportion is not known. The purely theoretical assumption that the pentosans represented by the formula $(C_5H_8O_4)_n$ become pentoses, $(C_5H_{10}O_5)_n$, by hydrolysis, and these in turn furfurol, $(C_5H_4O_2)_n$, would fix the proportion of furfurol to pentosan as 1 to 1.38. Actually the proportion is much greater, since, by the rather destructive process by which the pentosans are converted into furfurol, the theoretical amount is far from realised. For the present purposes of this paper, however, it is sufficient to regard the percentages of furfurol as representing the pentosans part for part, although in some respects this undoubtedly makes too low a showing.

Referring to the analyses, it appears that "Hans" consumed a total amount of pentosans equivalent to 24.768 grams of furfurol, of which 10.172 grams were voided, and 14.596 grams, or 58.93 per cent., were digested.

"Max" consumed the equivalent of 15.862 grams of furfurol, of which 5.955 were voided, and 9.907 grams, or 62.46 per cent., were digested.

An interesting result of these analyses is the showing that, while the pentosans made up 10.25 per cent. of the nitrogen-free extract of the food, this proportion was increased to 27.53 and 25.68 per cent. in the dung, and yet the ordinary digestion experiment takes no cognisance of this change in relative composition.

Following the first period was a preliminary feeding with bran alone during eight days, preparatory to the second period of six days. During this period "Hans" consumed 415 grams of bran and voided 172.3 grams of dung. Following are the analytical data:

	Bran.	Dung.
Moisture,	11.06 per cent.	14.22 per cent.
Ash,	7.40	9.50
Fibre,	9.91	19.27
Protein,	16.00	11.00
Ether extract,	4.36	2.34
N-free extract,	51.27	43.67
Furfurol obtained,	7.16	10.59
Pentosans (= furfurol × 1.38),	10.88	14.61
Proportion of pentosans in N-free extract,	21.22	33.46

In this period "Hans" consumed pentosans equivalent to 29.743 grams of furfurol, of which 18.247 grams were voided and 11.496 grams were digested. The proportion of pentosans in the nitrogen-free extract of the food (21.22 per cent.) was increased to 33.46 per cent. in the dung.

These results show that the pentosans are, to a marked degree, less digestible than the true carbohydrates, with which they have been indiscriminately classified. In the first period about 60 per cent. was digested, but in the second period, when the proportion of nitrogenous to carbonaceous matter was considerably increased, the pentosans did not seem able to supply the lack of carbohydrates and were themselves less than 40 per cent. digestible. Perhaps the most important result is that indicating the difference in composition between the "nitrogen-free extract" of the food and that of the dung. In digestion experiments these are assumed to be of the same character and the diminution in amount after passing the digestive tract is charged up roundly to the digestibility of the carbohydrates, whereas the digestive action has been selective and only certain constituents of the nitrogen-free extract have been removed, while others remain wholly or in part unchanged. No comparison of the analytical data is complete which fails to take into account the changed composition of the nitrogen-free extract.

These somewhat meagre data are submitted here for their sug-

gestiveness in a field in which little has been done, and also as illustrating the desirability of some analytical method more specific than the one now in use for the control of food valuations and digestion experiments.

CARBON DIOXIDE IN THE URINE.

By T. C. Van Nüys and R. E. Lyons.

To what is the alkalinity of normal urine ordinarily due? The student who would seek a solution of this question in medical literature will find the subject evaded, or the statement made that the urine is alkaline from the presence of the carbonates of the metals of the alkalies.

Our attention was first directed to this subject in preparing chemically pure normal urates of potassium and sodium ($C_5H_2N_4K_2O_3$, $C_5H_2N_4Na_2O_3$). We found that these salts are intensely alkaline in reaction, and knowing that the uric acid in normal urine is occasionally combined with these metals as normal urates, we were led to believe that the alkalinity of normal urine is due in part to the presence of normal urates, and that carbon dioxide in combination is not necessarily a constituent of normal urine, otherwise from urine distinctly alkaline in reaction, acid urates would separate. In order that in our researches an error might not be committed, we studied the properties of the normal urates of potassium and sodium.

Properties of the normal urates.—When either salt is dissolved in distilled water, the solution is intensely alkaline, not differing in this respect from strong solutions of either the hydrates or the carbonates of potassium and sodium.

On passing a current of carbon dioxide through a concentrated solution of either salt a white precipitate forms, which is at first the acid urate, $C_5H_3N_4KO_3$ or $C_5H_3N_4NaO_3$.

A strong solution of either normal salt yields a precipitate of the acid urate when treated with calcium acid phosphate, $CaH_4(PO_4)_2$.

Properties of the acid urates of potassium and sodium.—On introducing carbon dioxide into a concentrated aqueous solution of potassium or sodium acid urate, uric acid slowly separates. A strong solution of sodium hydrogen carbonate brings about decomposition of the acid urates in the same manner. The acid urate of either metal in aqueous solution is decomposed by means of calcium acid phosphate with the liberation of uric acid. On dissolving 90 mg. of the acid urate of sodium in 100 cc. distilled water and adding 300 mg. calcium acid phosphate, uric acid begins to separate in 8 minutes. If, however, 3 grams of pure urea be dissolved in the water with the acid urate before the acid phosphate is introduced, the decomposition of the acid urate does not begin within 20 minutes. The temperature at which the reaction took place was 16°- 19° C.

Deportment of the acid phosphates and carbonates.—When a solution of the acid phosphate of sodium or calcium is introduced into a solution of either the mono- or dicarbonate of potassium or sodium, carbon dioxide is liberated, and if sufficient acid phosphate be introduced the solution becomes acid in reaction. The acid sulphate of potassium or of sodium acts in the same manner. Although the acid urates of potassium and sodium contain each an atom of hydrogen which is displaceable by a metal, yet these salts are neutral or *very* slightly acid in reaction.

From the properties of the salts above enumerated we were led to believe that carbon dioxide in acid urine is always in the free state, and never in combination; and that as di- and basic potassium or sodium phosphates, as well as the normal urates of these metals, are intensely alkaline in reaction, the carbon dioxide is in all probability not in combination in moderately alkaline urine, but is combined in urine strongly alkaline.[1]

To determine this question, the carbon dioxide in the urine of one of us (L.) was estimated after employing (1) a mixed diet, (2) a vegetable diet, (3) after ingesting large doses of the neutral tartrate of sodium, $C_4H_4Na_2O_6$.

The following are the quantities of carbon dioxide estimated in the total urine of periods of 24 hours, for six consecutive days, with a mixed diet. The urine was acid in reaction during the whole time, 6 days:

[1] Neubauer states in his "Analyse des Harns" (8th edition, p. 106-7) that in acid urine, a part of the bases are in the form of bi-carbonates—hence carbon dioxide in combination.

First day, ...	0.64 gram CO_2.
Second day, ...	0.49 " "
Third day, ...	0.60 " "
Fourth day, ...	0.56 " "
Fifth day, ...	0.45 " "
Sixth day, ...	0.79 " "

Average for each period, 0.588 gram CO_2.

With a diet distinctly vegetable, urine strongly alkaline in reaction, the carbon dioxide increased, but when the urine was rendered acid no effervescence of carbon dioxide occurred. The basic phosphates were precipitated. The following quantities of carbon dioxide were determined in the urine of each period of 24 hours:

First day, ...	1.20 grams CO_2.
Second day, ...	1.16 " "
Third day, ...	0.93 gram "

Average for each period, 1.09 grams CO_2.

By ingesting 10 to 15 grams neutral sodium tartrate in 24 hours, the urine became strongly alkaline in reaction. During two periods of 48 hours each, two consecutive days, the neutral tartrate of sodium was taken in large doses.

The following are the quantities of the salt taken, and the number of grams of carbon dioxide in the urine of 24 hours:

First period 48 hours following "mixed diet."	Grams $C_4H_4Na_2O_6$ taken in 24 hours.	Grams CO_2 in urine of 24 hours.
1st day,	10	1.42
2d "	10	1.65
Second period 48 hours following vegetable diet.		
1st day,	15	1.30
2d "	15–17	2.67

From the results it is seen that in acid urine a relatively small quantity of carbon dioxide was found; that with a vegetable diet more carbon dioxide appeared in the urine; and that with large doses of sodium neutral tartrate the urine became alkaline, which was in part due to carbonates, as the urine effervesced slightly on the addition of an acid.

When the phosphoric, sulphuric and uric acids were present in the form of normal or basic salts, and as the blood was strongly alkaline by the presence of an unusual quantity of sodium bicar-

bonate, either sodium hydrate would necessarily appear in the urine, or carbon dioxide be combined with the excess of sodium, as was the case. It is a well recognised fact that the kidneys are the only emunctories through which notable quantities of the metals of the alkalies are eliminated.[1]

To transform the average quantities of phosphoric and uric acids in acid compounds in the urine of 24 hours into basic, or normal, salts without combined carbon dioxide, a relatively large quantity of sodium hydrate would be required, as is readily shown by the following table:

Quantity of acid salts in grams in the urine in 24 hours.	Acid Salts in the Urine in 24 Hours.
3.2634	$CaH_4(PO_4)_2 + 2CaCl_2 + 4NaOH \overset{(2.2506)}{=} Ca_3(PO_4)_2 + 4NaCl + 4H_2O.$
1.1146	$NaH_2PO_4 + 2NaOH \overset{(0.7430)}{=} Na_3PO_4 + 2H_2O.$
2.20408	$NaHSO_4 + NaOH \overset{(0.7346)}{=} Na_2SO_4 + H_2O.$
0.9046	$C_5H_3NaN_4O_3 + NaOH \overset{(0.1904)}{=} C_5H_2Na_2N_4O_3 + H_2O.$

The numbers in parenthesis over the NaOH are the quantities in grams of the alkali required to transform the acid salts into normal or basic salts. By adding these numbers it is found that to render alkaline the quantity of urine secreted in 24 hours, containing the average quantities of acids and bases, 3.9186 grams sodium hydrate are required.

In this connection it is seen that 2.9852 grams sodium hydrate of the total quantity (3.9186) are utilised in transforming the acid phosphate of calcium (including the equivalent of acid phosphate of magnesium) and the acid sulphate of sodium (including the equivalent of acid sulphate of potassium) without imparting alkalinity to the urine. The remainder, 0.9334 gram sodium hydrate, forms intensely alkaline salts. It is, however, doubtful if it ever occurs that all of the phosphoric, sulphuric and uric acids in the urine pass into acid compounds before ammonia makes its appearance in abnormal quantities.

From this table it is seen that in cases where the urine is strongly acid, and it is desired to render the urine alkaline by medication, small quantities of the tartrates, or acetates of sodium,

[1] Salkowsky: Centrbl. Med. Wiss., 1871, p. 289. Ref. Ztschr. anal. Chem. **10**, 378.

or of potassium, will, in all probability, fail to accomplish the desired result. With the acid phosphates and sulphates the normal urates cannot long remain. When in distilled water, in quantities in which they usually are in acid urine, they decompose normal urates in a few minutes, but by the presence of urea and other bodies in urine the action is retarded. Owing to this, urine, at first strongly acid from the presence of the acid phosphates and sulphates, although when cooled to ordinary temperatures, often has no sediment; but after the lapse of a few hours a heavy sediment of acid urates forms, and as the acid urates are scarcely acid in reaction, the urine by this change becomes less acid in reaction. The acid urates remaining in solution are slowly acted upon by the acid salts yet remaining. Probably the retarded action is due to the dilution of the acid salts. The reaction of the acid salts with the carbonates is so much more energetic that the latter would certainly be decomposed in the urine while yet in the bladder.

When the urine is alkaline from the presence of normal urates and basic, or "neutral," phosphates of the metals of the alkalies, carbon dioxide cannot exist firmly combined unless the metals of the alkalies are in quantities greater than sufficient to saturate the uric and phosphoric acids; otherwise uric acid, or acid urates of the metals of the alkalies, would separate as a sediment with the basic phosphates of calcium and magnesium. As the matter stands, however, there is no evidence that carbon dioxide may not be loosely combined with bases in alkaline urine, but not in a degree sufficient to cause the separation of the acid urates, or uric acid.

It is a well recognised fact in chemical science that when an equivalent of an acid is added to a normal salt in solution, the acid added, if it form a soluble salt with the base, does not set free the combined acid, although the acid added may be considered the stronger acid of the two. The base will be divided between the acids in certain proportions. Volatility of a product, however, is a modifying factor in the case. Owing to the fact that carbon dioxide exerts, in the presence of acid salts, dissociation-pressure, which is greater in degree than the attraction it has for bases, normal urates are not decomposed by it. However, in the absence of acid salts in the urine, according to the law which governs the relative affinity of acids for bases, there is no evidence based on experiment to disprove the hypothesis that carbon

dioxide may be, in limited quantity, feebly combined with bases associated with phosphoric, sulphuric, and uric acids in alkaline urine, but not sufficiently combined to set free either acid urates or uric acid. If the latter were true, acid urates of potassium and sodium and free uric acid would often be a sediment in alkaline urine, which is never the case.

Admitting the hypothesis that carbon dioxide may be feebly combined in urine which is alkaline but does not contain bases in quantities exceeding the saturating capacity of the acids present, with the exception of carbon dioxide, then we can explain why in our researches we found that carbon dioxide was in increased quantities in urine slightly alkaline from a vegetable diet.

From our investigations we conclude:

1st. Combined carbon dioxide is not ordinarily a constituent of normal urine.

2d. When carbon dioxide does appear in the urine combined, it is owing to excessive alkalinity of the blood when it is induced to combine with the hydrates of potassium and sodium, which would otherwise appear in the urine. The case is analogous to that of the neutral or even acid condition of the blood when ammonia appears in abnormal quantity, combined with acids.[1]

3d. Alkalinity of normal urine, unless excessive in degree, is caused by di- or tri-basic potassium, or sodium phosphates, and by normal urates of potassium and sodium.

CHEMICAL LABORATORY OF THE INDIANA UNIVERSITY, *November*, 1891.

[1] Frey: Centrbl. Med. Wiss., 1872, p. 833. Kurtz: Ueber Entziehung von Alkalien aus dem Thierkörper, Inaug. Diss., Dorpat, 1874. Walter: Archiv. f. exper. Pathologie u. Phar. **7**, 148. Gathgens: Ztschr. physiol. Chem. **4**, 36-54. E. Hallervorden: Arch. exper. Path. **12**, 237-275.

Contributions from the Sheffield Biological Laboratory of Yale University.

A STUDY OF THE PROTEIDS OF THE CORN OR MAIZE KERNEL.

By R. H. CHITTENDEN, Ph. D., *Professor of Physiological Chemistry in Yale University*, and THOMAS B. OSBORNE, Ph. D., *Chemist at the Connecticut Agricultural Experiment Station.*

(Continued from p. 552, Vol. 13.)

II.—PROTEIDS SOLUBLE BOTH IN WATER AND IN DILUTE SALT SOLUTIONS.

An aqueous extract of corn meal, as well as a sodium chloride extract, contains in addition to the globulins already described more or less proteid matter soluble in water alone and having the general properties of ordinary albumin and proteose. These bodies can be detected, either in the original extract after the complete removal of all globulin, or better in the ammonium-sulphate precipitate of the mixed proteids, after the globulins and their alteration-products have been entirely separated by dialysis and filtration.

Of albumin-like bodies there would appear to be two present, both more or less coagulable by heat, but unlike in chemical composition. Moreover, one is precipitable by the addition of dilute acetic or hydrochloric acid to a 10 per cent. sodium-chloride solution, after the globulins have been entirely removed, while the other remains in solution and can be advantageously separated only by coagulation of the neutralised fluid. From the albumin-free solution, the proteose can be separated by saturation with sodium chloride and addition of a little acetic, or hydrochloric acid.

An aqueous solution containing these water-soluble proteids is precipitated on saturation with ammonium sulphate, and on addition of alcohol, but not by saturation with sodium chloride. Addition of 0.2-per cent. hydrochloric acid or 30-per cent. acetic acid likewise gives no precipitate. Heated gradually, an aqueous solution of these proteids becomes turbid at about 46°, with separation of a flocculent precipitate at 60°. Between 60° and 70° a fairly large coagulum separates. The fluid again becomes turbid about 85°, and on boiling, a slight coagulum appears which gradually increases as the boiling is continued. In fact, it is very diffi-

cult to make a complete coagulation. The solution may be evaporated nearly to dryness, the residue taken up in water and filtered, and then on boiling this solution for some time an additional coagulum may appear. Indeed, there is every evidence of some kind of transformation in the process of coagulation, or possibly it may be that we have to deal simply with a body very slowly, or incompletely, coagulable by heat, like some forms of phyt-albumose.

Preparation A.—The proteids precipitated from a sodium-chloride extract of 5 kilos. of corn meal, by means of ammonium sulphate, were dissolved in water and 10-per cent. solution of sodium chloride, and dialysed until every trace of globulin and soluble salts had been removed. To the clear neutral fluid thus obtained, which gave no precipitate whatever on the addition of dilute acid or on saturation with sodium chloride, pure, crystallised salt was added in such quantity that the solution contained 10 per cent. of sodium chloride, after which the clear fluid was rendered slightly acid with 0.2-per cent. hydrochloric acid. The precipitate thus produced was filtered off, treated with water in which, or in the slightly acid fluid which resulted, it was mainly soluble, and the solution carefully neutralised with a few drops of very dilute sodium carbonate. This gave rise to an abundant precipitate which was filtered off, washed thoroughly with water, alcohol and ether, weighing, when air-dry, 2.48 grams (Albumin A[1]). This substance, when first precipitated by neutralisation, was very readily soluble in dilute sodium carbonate, but after becoming dry it was wholly insoluble in the dilute alkaline fluid.

This description affords a very good illustration of the readiness with which some of these vegetable proteids undergo change by mere contact with dilute acids or alkalies. Evidently, the addition of a little 0.2-per cent. acid to the salt solution of these proteids gives rise to an acid compound of one of the albumins insoluble in salt solution (10-per cent.), but soluble in water or, rather, in the slightly acid fluid. Withdrawal of the acid, however, by neutralisation with a few drops of very dilute sodium carbonate, yields not the original albumin, but apparently an insoluble acid-albumin; a reaction more characteristic of a globulin than of a genuine albumin.

The 10-per cent. sodium-chloride solution, from which the above albumin was precipitated by the addition of 0.2-per cent.

hydrochloric acid, was heated to boiling, when there resulted a coagulum which, after being washed with hot water until free from salt, and then with alcohol and ether, weighed air-dry, 1.03 grams (Albumin A^3).

On boiling the filtrate from this latter coagulum, no further precipitate could be obtained, but saturation of the slightly acid fluid with salt gave a considerable precipitate, readily soluble in water. The substance thus precipitated was therefore dissolved in water and dialysed until the sodium chloride was entirely removed. The salt-free solution was then evaporated to dryness on a water-bath. As the solution became concentrated, a portion of the proteid separated as a scum or skin on the surface of the fluid, eventually making an insoluble coagulum. On treating the dried residue with water, still more insoluble matter appeared, showing that either all of the coagulable albumins (Albumins A^1 and A^2) had not been removed from the fluid, or else that in the process of treatment changes were going on by which new coagulable matter was being formed. Eventually, however, by evaporating the filtered fluid to dryness several times and taking up the residue in water, there resulted a solution of a proteid body which showed no signs of coagulation, even on long-continued heating, and which yielded a gummy precipitate on the addition of absolute alcohol. This proteose-like body was, however, obtained in very small quantity—only about 0.3 gram—and might be considered as possibly formed by the hydrolytic action of the repeated evaporations, etc.

On the other hand, it might perhaps be claimed with equal plausibility that the slow coagulations witnessed above were the result of a regressive metamorphism of a proteose normally present in the corn-kernel.

The two albumins, A^1 and A^2, were dried at 110° C. and analysed with the following results:

Analysis of Albumin A^1.

I. 0.3828 gram substance gave 0.2355 gram H_2O = 6.84 per cent. H, and 0.7398 gram CO_2 = 52.71 per cent. C.

II. 0.3454 gram substance gave 43.4 cc. N at 3.0° C. and 761.7 mm. pressure = 15.64 per cent. N.

III. 0.3185 gram substance gave 39.4 cc. N at 2° C. and 768.5 mm. pressure = 15.60 per cent. N.

IV. 0.3292 gram substance gave 0.0010 gram ash = 0.30 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	52.86	..	..	52.86
H	6.86	..	..	6.86
N	..	15.69	15.65	15.67
S	..	..	.. }	24.61
O	..	..	.. }	
				100.00

Analysis of Albumin A[2].

I. 0.2355 gram substance gave 0.1430 gram H_2O = 6.76 per cent. H, and 0.4464 gram CO_2 = 51.72 per cent. C.

II. 0.3498 gram substance gave 45.9 cc. N at 3° C. and 758.5 mm. pressure = 16.27 per cent. N.

III. 0.3214 gram substance gave 0.0013 gram ash = 0.40 per cent.

Percentage Composition of the Ash-free Substance.

			Average.
C	51.93	..	51.93
H	6.79	..	6.79
N	..	16.33	16.33
S	..	.. }	24.95
O	..	.. }	
			100.00

Preparation B.

Another series of similar products was made as follows: 6.5 kilos. of finely ground corn were extracted first with water and then with 10-per cent. salt solution. From these two extracts the proteids were precipitated by saturation with ammonium sulphate, the precipitates dissolved separately, so far as possible, in water and 10-per cent. salt solution, and the globulins separated by thorough dialysis. In the two filtrates, wholly free from globulin, the addition of an equal volume of 20-per cent. salt solution and a little 0.2-per cent. hydrochloric acid produced a flocculent precipitate, considerably heavier in the aqueous extract than in the sodium-chloride extract. As the two precipitates, however, were apparently the same, they were united and dissolved, so far as possible, in water. In this case, unlike the preceding experiment, a large proportion of the precipitate did not dissolve in the water added, apparently because the fluid was not sufficiently acid. This insoluble portion, after being washed with

water, was therefore dissolved in a little 0.2-per cent. hydrochloric acid and the solution carefully neutralised with dilute sodium carbonate, by which the substance was reprecipitated. After being washed thoroughly with water, alcohol and ether, it weighed, air-dry, 2.67 grams (Albumin B^1).

On analysis, after drying at 110° C., it yielded the following results:

Analysis of Albumin B^1.

I. 0.3274 gram substance gave 0.1992 gram $H_2O = 6.75$ per cent. H, and 0.6369 gram $CO_2 = 53.05$ per cent. C.

II. 0.3133 gram substance gave 0.1900 gram $H_2O = 6.74$ per cent. H, and 0.6081 gram $CO_2 = 52.92$ per cent. C.

III. 0.4413 gram substance gave 54.8 cc. N at 20° C. and 762.1 mm. pressure = 15.53 per cent. N.

IV. 0.4758 gram substance gave 0.0048 gram ash = 1.01 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	53.58	53.48	..	53.53
H	6.82	6.81	..	6.82
N	..	..	15.69	15.69
S	..	..	.. }	23.96
O	..	..	.. }	
				100.00

The two original acid filtrates, from which the above albumin was separated, were in this preparation directly saturated with sodium chloride, and the precipitate of the residual albumin and proteose filtered off and dissolved in water. The resultant solutions were united, neutralised and dialysed until the salts were entirely removed. At the end of the dialysis, a small amount of substance was found adhering to the walls of the dialyser, not, however, sufficient in quantity to do anything with. On evaporation of the filtered fluid to half its volume considerable coagulum formed, which was washed with water, alcohol and ether, weighing, when air-dry, 1.32 grams (Albumin B^2). On further evaporation of the mother-liquor containing the proteose an additional coagulum formed, which was added to the preceding.

This preparation, dried at 110° C., gave on analysis the following results:

Analysis of Albumin B^2.

I. 0.2387 gram substance gave 0.1453 gram $H_2O = 6.76$ per cent. H, and 0.4547 gram $CO_2 = 51.95$ per cent. C.

II. 0.3546 gram substance gave 47.6 cc. N at 3° C. and 751.8 mm. pressure = 16.49 per cent. N.

III. 0.3868 gram substance gave 0.0008 gram ash = 0.21 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	52.06	..	..	52.06
H	6.77	..	..	6.77
N	..	16.53	..	16.53
S	..	..	.. }	24.64
O	..	..	.. }	
				100.00

In the filtrate from which this last body was obtained there still remained some coagulable matter, which was finally completely removed by careful heating on a water-bath. The concentrated and perfectly neutral fluid was then precipitated with absolute alcohol, and the resultant proteose collected and washed with alcohol and ether.

This substance, like the soluble proteoses formed from animal proteids, was especially characterised by extreme solubility in water, non-coagulability by heat, etc. It was precipitated by acetic acid and potassium ferrocyanide, by alcohol, phosphotungstic acid, etc., and gave the usual proteid reactions with Millon's reagent, and with cupric sulphate and potassium hydroxide.

Dried at 110° C. until of constant weight, the product, separated as just described, gave on analysis the following results:

Analysis of Proteose B.

I. 0.3390 gram substance gave 0.1952 gram H_2O = 6.40 per cent. H, and 0.6154 gram CO_2 = 49.51 per cent. C.

II. 0.3409 gram substance gave 0.1993 gram H_2O = 6.49 per cent. H, and 0.6158 gram CO_2 = 49.27 per cent. C.

III. 0.3326 gram substance gave 41.3 cc. N. at 2.5° C. and 760.9 mm. pressure = 15.49 per cent. N.

IV. 0.2984 gram substance gave 37.4 cc. N at 4° C. and 758.5 mm. pressure = 15.49 per cent. N.

V. 0.2784 gram substance, fused with $KOH + KNO_3$, gave 0.0520 gram $BaSO_4$ = 2.57 per cent. S; deducting 0.25 for S in the ash = 2.32 per cent. S.

VI. 0.4206 gram substance gave 0.0120 gram ash = 2.42 per cent.

Percentage Composition of the Ash-free Substance.

						Average.
C	50.74	50.50	..	..	..	50.62
H	6.56	6.65	..	..	..	6.61
N	..	..	15.88	15.88	..	15.88
S	..	..	..	..	2.37	2.37
O	..	..	..	..	..	24.52
						100.00

Preparation C.

These same bodies were prepared again, on a somewhat larger scale, from 25 kilos. of finely ground corn. The process was as follows: The meal was extracted directly with an abundance of 10-per cent. salt solution, and the proteids precipitated collectively by saturation of the fluid with ammonium sulphate. The precipitate was dissolved in water and salt solution, and the fluid dialysed about three weeks, until the salts were entirely removed and the globulins completely separated.

The salt-free solution, containing the albumins and proteose, was then treated with sodium chloride until the mixture contained 10 per cent. of salt, after which 0.2-per cent. hydrochloric acid was added until the precipitation was complete. The albumin so separated was filtered off and treated with water, in which about four-fifths of it dissolved. The residue, however, was dissolved in a little 0.2-per cent. hydrochloric acid and the two solutions united, and dialysed until free from chlorides. At the end of the dialysis the fluid was perfectly neutral, and the albumin (obviously altered), or a portion of it, was found precipitated in the parchment tube, the same as on neutralisation of the slightly acid fluid described in the previous preparations, while in the solution was found considerable non-coagulable proteose which must have been carried down with the albumin. The precipitate (Albumin C') was filtered off, washed thoroughly with water, alcohol and ether, and dried at 110° C. for analysis. Air-dry, it weighed 3.14 grams.

Analysis of Albumin C'.

I. 0.3459 gram substance gave 0.2102 gram H_2O = 6.75 per cent. H, and 0.6714 gram CO_2 = 52.93 per cent. C.

II. 0.3649 gram substance gave 0.2222 gram H_2O = 6.77 per cent. H, and 0.7065 gram CO_2 = 52.81 per cent. C.

III. 0.3546 gram substance gave 43 cc. N at 774.0 mm. pressure = 15.35 per cent. N.

IV. 0.6957 gram substance fused with $KOH + KNO_3$ gave 0.0750 gram $BaSO_4 = 1.48$ per cent. S.

V. 0.4331 gram substance gave 0.0016 gram ash = 0.37 per cent.

Percentage Composition of the Ash-free Substance.

					Average.
C	53.12	53.00	..	..	53.06
H	6.78	6.80	..	..	6.79
N	..	..	15.41	..	15.41
S	..	..	..	1.48	1.48
O	..	..	..	..	23.26
					100.00

The proteose precipitated with the above albumin was separated from the concentrated solution, after removal of all coagulable matter, by precipitation with absolute alcohol. It weighed, air-dry, 2.5 grams and gave on analysis, after drying at 110° C., the following results:

Analysis of Proteose C[1].

I. 0.3131 gram substance gave 0.1903 gram $H_2O = 6.75$ per cent. H, and 0.5717 gram $CO_2 = 49.80$ per cent. C.

II. 0.3783 gram substance gave 0.2276 gram $H_2O = 6.69$ per cent. H, and 0.6873 gram $CO_2 = 49.55$ per cent. C.

III. 0.3397 gram substance gave 43.5 cc. N at 3° C. and 770.7 mm. pressure = 16.13 per cent. N.

IV. 0.7246 gram substance fused with $KOH + KNO_3$ gave 0.0837 gram $BaSO_4 = 1.58$ per cent. S.

V. 0.4632 gram substance gave 0.0131 gram ash = 2.83 per cent.

Percentage Composition of the Ash-free Substance.

					Average.
C	51.25	51.00	..	..	51.13
H	6.94	6.88	..	..	6.91
N	..	..	16.59	..	16.59
S	..	..	..	1.62	1.62
O	..	..	..	..	23.75
					100.00

The original filtrate from the precipitate produced by dilute hydrochloric acid in the presence of 10-per cent. sodium chloride was dialysed until nearly free from salt, and then, being perfectly neutral to test-papers, was concentrated to one-third its volume and filtered from the coagulum which resulted. This coagulum

(Albumin C^2) was washed thoroughly with water, alcohol and ether, and after being dried at 110° C. was analysed. Air-dry it weighed 2.28 grams.

Analysis of Albumin C^2, First Coagulum.

I. 0.3226 gram substance gave 0.1927 gram H_2O = 6.64 per cent. H, and 0.6092 gram CO_2 = 51.50 per cent. C.

II. 0.3293 gram substance gave 0.1985 gram H_2O = 6.69 per cent. H, and 0.6195 gram CO_2 = 51.31 per cent. C.

III. 0.3737 gram substance gave 46.3 cc. N at 3° C. and 774.2 mm. pressure = 15.68 per cent. N.

IV. 0.4015 gram substance gave 0.0038 gram ash = 0.94 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	51.97	51.78	..	51.88
H	6.70	6.75	..	6.73
N	..	..	15.89	15.89
S	..	..	.. }	25.50
O	..	..	.. }	
				100.00

The filtrate from the above coagulum was concentrated still further, without giving any appreciable coagulum, then saturated with salt and precipitated by the addition of 0.2-per cent. hydrochloric acid. The precipitate was dissolved in water, dialysed until the salt had been entirely removed, and then evaporated to dryness on the water-bath. During this last evaporation a considerable coagulum formed, which was collected, washed, dried and analysed. It weighed 1.22 grams (Albumin C^2, second coagulum).

Analysis of Albumin C^2, Second Coagulum.

I. 0.4488 gram substance gave 0.2600 gram H_2O = 6.44 per cent. H, and 0.8224 gram CO_2 = 49.98 per cent. C.

II. 0.3050 gram substance gave 41.8 cc. N at 3° C. and 755.8 mm. pressure = 16.93 per cent. N.

III. 0.3769 gram substance gave 0.0077 gram ash = 2.04 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	51.02	..	..	51.02
H	6.57	..	..	6.57
N	..	17.28	..	17.28
S	..	..	.. }	25.13
O	..	..	.. }	
				100.00

From the concentrated filtrate from this second coagulum, a small amount of proteose was separated by addition of absolute alcohol. Dried at 110° and analysed, it gave the following results:

Analysis of Proteose C².

I. 0.3666 gram substance gave 0.2065 gram H_2O = 6.26 per cent. H, and 0.6435 gram CO_2 = 47.87 per cent. C.

II. 0.3333 gram substance gave 0.1901 gram H_2O = 6.34 per cent. H, and 0.5934 gram CO_2 = 48.55 per cent. C.

III. 0.3654 gram substance gave 46.3 cc. N at 3° C. and 768.9 mm. pressure = 15.93 per cent. N.

IV. 0.4266 gram substance gave 0.0159 gram ash = 3.72 per cent.

Percentage Composition of the Ash-free Substance.

				Average.
C	49.72	50.42	..	50.07
H	6.50	6.58	..	6.54
N	..	..	16.54	16.54
S	..	..	..	26.85
O	..	..	..	
				100.00

Preparation D.

Another experiment after the same order as the preceding was carried out without, however, yielding sufficient of any one product for analysis, except of the albumin coagulable by heat present in the filtrate from the precipitate produced by 10-per cent. salt solution and dilute acid.

This product (Albumin D²) was analysed for the sake of additional confirmatory evidence, with the following results :

Analysis of Albumin D², Coagulum.

I. 0.4274 gram substance gave 0.2584 gram H_2O = 6.71 per cent. H, and 0.8055 gram CO_2 = 51.39 per cent. C.

II. 0.3735 gram substance gave 0.2278 gram H_2O = 6.77 per cent. H, and 0.7076 gram CO_2 = 51.66 per cent. C.

III. 0.3739 gram substance gave 49.8 cc. N at 17.3° C. and 757 mm. pressure = 15.67 per cent. N.

IV. 0.3783 gram substance gave 51.1 cc. N at 18.2° C. and 755.1 mm. pressure = 15.80 per cent N.

V. 0.3450 gram substance gave 0.0013 gram ash = 0.38 per cent.

Percentage Composition of the Ash-free Substance.

					Average.
C	51.58	51.84	..	..	51.71
H	6.73	6.79	..	..	6.76
N	..	..	15.72	15.85	15.78
S, O	..	..	..	..	25.75
					100.00

The relationship in composition of these several products can be seen from the following table:

Albumin Precipitated by Salt and Acid.

	A^1.	B^1.	C^1.
C	52.86	53.53	53.06
H	6.86	6.82	6.79
N	15.67	15.69	15.41
S	24.61	23.96	1.48
O			23.26

Albumin Coagulated by Heat.

	A^2.	B^2.	C^2, 1st.	C^2, 2d.	D^2.
C	51.93	52.06	51.88	51.02	51.71
H	6.79	6.77	6.73	6.57	6.76
N	16.33	16.53	15.89	17.28	15.78
S, O	24.95	24.64	25.50	25.13	25.75

Proteose.

	B.	C^1.	C^2.
C	50.62	51.13	50.07
H	6.61	6.91	6.54
N	15.88	16.59	16.54
S	2.37	1.62	26.85
O	24.52	23.75	

We are so firmly convinced that these bodies are, in part at least, the products of changes induced by the several steps incidental to their separation, that we are loth to draw any very definite conclusions as to their true chemical composition. By this we do not mean that these three series of products are wholly artificial. Bodies of the general nature of the albumins here indicated unquestionably exist in the corn-kernel. As already stated, an aqueous solution of the corn proteids, entirely freed from globulins, gives a coagulum between 60° and 70°, and another one between 85° and 100°, thus implying the presence of two distinct bodies. It may

possibly be assumed that the albumin precipitated by salt and acid is simply a portion of the albumin separated later by coagulation; that this partial precipitation is simply another illustration of the incompleteness characteristic of the separation of these albumins, as witnessed, for example, in the gradual and incomplete coagulation of the above albumin by heat; and further, that the difference in chemical composition between the first and second series of products is simply due to their alteration by the processes made use of. Yet we can hardly consider this the true view. The peculiar heat-coagulation phenomena of the original aqueous solution, before any separations were attempted, lend favor to the view that at least two coagulable albumins are present. On the other hand, the incompleteness of the coagulation at any one point—the fact that more and more coagulum continues to form as the boiling is continued—points clearly to gradual changes, which, doubtless, leave their impression upon the products separated. Thus, in Preparation C, the two albumins coagulated by heat, C^2 1st and C^2 2d, should theoretically have the same composition, the only tangible difference being that the second coagulum required longer heating to bring about its separation, and yet it differs from its neighbor by 1.5 per cent. of nitrogen. Observations of this character, and others which we will not take space to detail, confirm us in the opinion that these soluble bodies are exceedingly prone to change, and doubtless the composition here given is only an approximation to the true make-up of the substances as they exist in the corn-kernel. At the same time, it may not be amiss to recall the fact that in the seed itself, in its various stages of growth and development, kindred changes are doubtless taking place among its natural proteid constituents. Whether the proteose separated by the above methods exists as such in the corn-kernel, or whether it is derived from the other proteids by the methods of separation, is likewise uncertain. A portion of it is unquestionably formed by the hydrolytic changes incidental to the separation of the coagulable proteids, and this favors the view that it is wholly an artificial product.

Further, a similar proteose-like body was directly prepared by heating to 80° C. one of the preceding globulins, dissolved in salt-solution. Again, the somewhat variable composition of the proteoses analysed suggests a mixture of two or more dissimilar proteoses, such as might be expected in an artificial production of the character indicated.

One point to be noted in connection with the proteose is its relatively low content of carbon; a point which is characteristic of most of the albumoses or proteoses formed by the action of the digestive ferments, both from animal and vegetable proteids.

III.—Proteid Matter Soluble in Alcohol, but Insoluble in Water and Salt-Solutions.

Under this head we have to deal with only one substance, viz. *Zein* or the "maize fibrin" of Ritthausen. The former name, originally given by Gorham[1] to this peculiar proteid found by him in *Zea mays*, seems especially appropriate, and we would suggest its adoption as a more fitting name than the term employed by Ritthausen. This body, as is well known, is especially characterised by its solubility in weak alcohol, and can be obtained by direct extraction of corn meal with 95-per cent. alcohol, preferably at 40°–60°C., or by extraction of the meal with warm alcohol after previous treatment with water, salt-solution, or both.

Several preparations were made under varying conditions as follows:

Preparation A.

2.5 kilos. of finely ground corn meal were first thoroughly extracted with cold water, after which the residue of meal was treated with 95-per cent. alcohol in sufficient quantity to have the water retained by the meal reduce the strength to about 75 per cent. The mixture was warmed for some hours at about 46° C., and finally filtered at approximately that temperature. The filtrate was concentrated on the water-bath at a temperature below 65° C. The residue of meal was again treated with 75-per cent. alcohol (4 litres) at 60°C. for several hours, and filtered while at that temperature. In all, five successive extractions were made after this fashion, the individual alcoholic extracts being evaporated separately, all at a low temperature. The last three extracts left but little residue on evaporation. As the first two extracts became concentrated the proteid separated as a tough, leathery, yellow-colored mass on the sides and bottom of the dish. It was cut up into small pieces and soaked for several days in cold absolute alcohol. On this first treatment of the proteid with absolute alcohol some little dissolved, presumably from dilution of the

[1] See Berzelius, Jahresbericht 2, (1822), p. 194.

alcohol with the water contained in the substance. This alcoholic extract was therefore concentrated to a syrup and the proteid precipitated by ether. It then had the appearance of a crumbly, pulverisable substance, and was easily ground to a powder under absolute alcohol. On slightly warming the alcohol, however, the substance melted and finally dissolved completely in the alcoholic fluid. On cooling this solution, the substance separated in a very gummy state.

The main portion of the proteid, which had been treated once with absolute alcohol, was treated with successive portions of cold absolute alcohol, as long as anything was dissolved by this reagent, after which it was treated with a mixture of one part of ether and two parts of absolute alcohol and, finally, was soaked in ether alone. After this treatment we were able to reduce it to a fine powder, when it was thoroughly extracted with ether for the complete removal of any adhering fat.

So prepared, the substance was only partially soluble in warm 75-per cent. alcohol, a portion of it during the foregoing process having been converted into an insoluble modification. This change from the soluble (in warm alcohol) to the insoluble form is liable to occur whenever the substance is heated with too watery alcohol, especially if the temperature approaches 100° C., or if the heating be long-continued. The soluble portion referred to above was therefore completely separated by repeated treatment with warm and with boiling dilute alcohol, and the insoluble portion ultimately washed with absolute alcohol and ether and dried at 110° C. for analysis.

The alcoholic solution of the soluble portion of the proteid was poured into about three volumes of water, by which the substance was precipitated in white flocks, which, however, soon commenced to unite and rise to the surface, eventually forming a dense cake. On heating this mass it continued to contract, squeezing out the water in large quantities. The substance, still containing considerable water, was next dissolved in warm 95-per cent. alcohol, the solution filtered, concentrated to about 400 cc. and again poured into a large volume of water, about 3 litres. This time the substance did not separate as before, but remained suspended in the form of a thick emulsion and was made to flock only on the addition of a little salt. It was then filtered off, washed with

water until free from chlorides, lastly with alcohol and ether and dried at 110° C. for analysis.

Analysis of Zein. Preparation A.—Soluble.

I. 0.3079 gram substance gave 0.2045 gram H_2O = 7.34 per cent. H, and 0.6226 gram CO_2 = 55.14 per cent. C.

II. 0.3453 gram substance gave 46.8 cc. N at 17.0° C. and 757.9 mm. pressure = 15.98 per cent. N.

III. 0.5310 gram substance fused with KOH + KNO_3 gave 0.0197 gram $BaSO_4$ = 0.51 per cent. S.

IV. 1.0210 grams substance fused with KOH + KNO_3 gave 0.0402 gram $BaSO_4$ = 0.54 per cent. S.

V. 1.0600 grams substance gave 0.0024 gram ash = 0.22 per cent.

VI. 1.0045 grams substance gave 0.0028 gram ash = 0.27 per cent.

Percentage Composition of the Ash-free Substance.

					Average.
C	55.27	..	..	..	55.27
H	7.35	..	..	..	7.35
N	..	16.01	..	..	16.01
S	..	..	0.51	0.54	0.53
O	..	..	..	..	20.84
					100.00

Analysis of Zein. Preparation A.—Insoluble.

I. 0.3210 gram substance gave 0.2094 gram H_2O = 7.24 per cent. H, and 0.6451 gram CO_2 = 54.80 per cent. C.

II. 0.4055 gram substance gave 0.2680 gram H_2O = 7.34 per cent. H, and 0.8170 gram CO_2 = 54.94 per cent. C.

III. 0.3171 gram substance gave 43.1 cc. N at 17.1° C. and 761.6 mm. pressure = 16.10 per cent. N.

IV. 0.3250 gram substance gave 43.7 cc. N at 16.8° C. and 763.5 mm. pressure = 15.98 per cent. N.

V. 0.5000 gram substance fused with KOH + KNO_3 gave 0.0221 gram $BaSO_4$ = 0.61 per cent. S.

VI. 0.9834 gram substance gave 0.0018 gram ash = 0.18 per cent.

VII. 0.2637 gram substance gave 0.0005 gram ash = 0.19 per cent.

Percentage Composition of the Ash-free Substance.

						Average.
C	54.90	55.04	..	..	..	54.97
H	7.25	7.35	..	..	..	7.30
N	..	..	16.01	16.13	..	16.07
S	..	..	..	..	0.61	0.61
O	..	..	..	..	..	21.05
						100.00

Preparation B.

2.5 kilos. of finely ground corn, which had been thoroughly extracted with 10-per cent. salt solution, were treated directly with warm 75-per cent. alcohol, until the alcohol ceased to dissolve anything further. The first alcoholic extract, on concentration, yielded the proteid—doubtless on account of the large amount of sodium chloride it contained—as a yellow, granular mass which could be broken quite readily. The residues from the following extracts, however, were of the same general nature as those described under Preparation A. All of the residues from the several extracts were united, washed with distilled water until the salt was entirely removed, then dissolved in warm 80-per cent. alcohol and the solution filtered to remove any insoluble matter present. The solution was next evaporated on a water-bath nearly to dryness and the residue pressed as dry as possible, yielding a yellow, elastic substance which could be pulled like molasses candy, but which was much more elastic and tough. Its elasticity was so great that it could be pulled into sheets several inches square and very thin. After continued kneading under absolute alcohol, it finally became brittle, a considerable portion of it passing into solution at the same time. After thorough extraction with absolute alcohol in this manner, it was soaked for some time in ether and then ground to a coarse powder. Like the preceding preparation, the proteid was now found only partially soluble in dilute alcohol. It was therefore separated into two portions by continued treatment with warm 80-per cent. alcohol, after first moistening the powdered product with a little water. The insoluble portion was washed with absolute alcohol and ether, and dried at 110° C. for analysis.

The alcoholic solution containing the soluble portion of the proteid was poured into three volumes of water, by which the zein was precipitated in white flocks, which gradually formed into a cake floating on the surface of the fluid. This was redissolved in 95-per cent. alcohol, and again precipitated as before. After a third precipitation in this manner, the substance was dissolved in 95-per cent. alcohol, the solution filtered, and the filtrate evaporated on the water-bath. Towards the end, absolute alcohol was added several times in order to prevent the substance from separating in consequence of the alcohol becoming too dilute. The

evaporation was finally carried to dryness, and the residue cut up into small pieces and thoroughly extracted with ether. A portion of this soluble zein, dried at 110° C. until of constant weight, was analysed with the following results:

Analysis of Zein. Preparation B.—Soluble.

I. 0.3252 gram substance gave 0.2132 gram H_2O = 7.28 per cent. H, and 0.6550 gram CO_2 = 54.92 per cent. C.

II. 0.2968 gram substance gave 0.1932 gram H_2O = 7.24 per cent. H, and 0.5985 gram CO_2 = 54.98 per cent. C.

III. 0.4193 gram substance gave 57.4 cc. N at 17.3° C. and 755.1 mm. pressure = 16.06 per cent. N.

IV. 0.3569 gram substance gave 49.5 cc. N at 18.4° C. and 755.1 mm. pressure = 16.20 per cent. N.

V. 0.5365 gram substance gave 0.0025 gram ash = 0.46 per cent.

VI. 0.4590 gram substance gave 0.0020 gram ash = 0.46 per cent.

VII. 1.0270 grams substance fused with KOH + KNO_3 gave 0.0423 gram $BaSO_4$ = 0.57 per cent. S.

VIII. 1.0093 grams substance fused with KOH + KNO_3 gave 0.0385 gram $BaSO_4$ = 0.52 per cent. S.

Percentage Composition of the Ash-free Substance.

							Average.
C	55.17	55.23	..	..	..	..	55.20
H	7.31	7.27	..	..	..	..	7.29
N	..	..	16.13	16.27	..	..	16.20
S	..	..	..	..	0.57	0.52	0.55
O	..	..	..	..	..	..	20.76
							100.00

The insoluble portion, after being dried at 110° C., gave the following results on analysis:

Analysis of Zein. Preparation B.—Insoluble.

I. 0.3562 gram substance gave 0.2290 gram H_2O = 7.14 per cent. H, and 0.7200 gram CO_2 = 55.12 per cent. C.

II. 0.4284 gram substance gave 0.2772 gram H_2O = 7.19 per cent. H, and 0.8660 gram CO_2 = 55.12 per cent. C.

III. 0.4203 gram substance gave 0.2708 gram H_2O = 7.15 per cent. H, and 0.8504 gram CO_2 = 55.17 per cent. C.

IV. 0.3733 gram substance gave 51.2 cc. N at 17.5° C. and 762.4 mm. pressure = 16.24 per cent. N.

V. 0.4449 gram substance gave 60.8 cc. N at 16.9° C. and 761.8 mm. pressure = 16.20 per cent. N.

VI. 0.5238 gram substance fused with KOH + KNO_3 gave 0.0245 gram $BaSO_4$ = 0.64 per cent. S.

VII. 0.7747 gram substance fused with $KOH + KNO_3$ gave 0.0350 gram $BaSO_4 = 0.62$ per cent. S.

VIII. 0.4675 gram substance gave 0.0021 gram ash $= 0.45$ per cent.

IX. 0.4705 gram substance gave 0.0020 gram ash $= 0.43$ per cent.

Percentage Composition of the Ash-free Substance.

								Average.
C	55.36	55.36	55.41	..	..	..	..	55.37
H	7.17	7.22	7.18	..	..	..	..	7.19
N	..	..	..	16.31	16.27	..	..	16.29
S	..	..	..	..	..	0.64	0.62	0.63
O	..	..	..	..	..	..	..	20.52
								100.00

Preparation C.

2.5 kilos. of corn meal, previously extracted with 5-per cent. ammonium chloride solution, were treated several times with warm 75-per cent. alcohol, and the alcoholic extract concentrated at a low temperature. The leathery-like residues left by evaporation of the alcohol were washed somewhat with water, then dissolved, so far as possible, in warm 80-per cent. alcohol, the clear fluid evaporated nearly to dryness, and the residue digested repeatedly with absolute alcohol and, lastly, with ether. On becoming air-dry, the substance was pulverised and again extracted with ether. It was then dissolved as completely as possible in 80-per cent. alcohol, after having been first gently warmed with a little water. A considerable quantity of the substance remaining insoluble, this was removed by decantation and filtration, the residue washed first with dilute alcohol, lastly with alcohol and ether, and dried at 110° C. for analysis. The alcoholic solution containing the soluble portion of the proteid was precipitated by being poured into water, a process which was repeated three times; after which the precipitated zein was digested with absolute alcohol and finally with ether, and a portion dried at 110° C. for analysis.

Analysis of Zein. Preparation C.—Soluble.

I. 0.3728 gram substance gave 0.2396 gram $H_2O = 7.14$ per cent. H, and 0.7520 gram $CO_2 = 55.01$ per cent. C.

II. 0.3587 gram substance gave 0.2305 gram $H_2O = 7.14$ per cent. H, and 0.7236 gram $CO_2 = 55.01$ per cent. C.

III. 0.4218 gram substance gave 58.0 cc. N at 17.2° C. and 759.6 mm. pressure $= 16.24$ per cent. N.

IV. 0.4085 gram substance gave 55.9 cc. N at 17.2° C. and 760.2 mm. pressure $= 16.17$ per cent. N.

V. 1.0375 grams substance fused with KOH + KNO_3 gave 0.0460 gram $BaSO_4$ = 0.61 per cent. S.

VI. 0.8267 gram substance fused with KOH + KNO_3 gave 0.0348 gram $BaSO_4$ = 0.58 per cent. S.

VII. 0.4610 gram substance gave 0.0008 gram ash = 0.17 per cent.

VIII. 0.5250 gram substance gave 0.0009 gram ash = 0.17 per cent.

Percentage Composition of the Ash-free Substance.

							Average.
C	55.10	55.10	..	..	..	..	55.10
H	7.15	7.15	..	..	..	..	7.15
N	..	..	16.26	16.19	..	..	16.22
S	..	..	..	..	0.61	0.58	0.60
O	..	..	..	..	..	..	20.93
							100.00

Analysis of Zein, Preparation C.—Insoluble.

I. 0.3885 gram substance gave 0.2518 gram H_2O = 7.20 per cent. H, and 0.7835 gram CO_2 = 54.99 per cent. C.

II. 0.3848 gram substance gave 0.2514 gram H_2O = 7.25 per cent. H, and 54.94 per cent. C.

III. 0.4964 gram substance gave 67.9 cc. N at 17.5° C. and 763.6 mm. pressure = 16.22 per cent. N.

IV. 0.4119 gram substance gave 57.0 cc. N at 17.7° C. and 760.6 mm. pressure = 16.33 per cent. N.

V. 0.5295 gram substance fused with KOH + KNO_3 gave 0.0240 gram $BaSO_4$ = 0.62 per cent. S.

VI. 0.5890 gram substance fused with KOH + KNO_3 gave 0.0273 gram $BaSO_4$ = 0.64 per cent. S.

VII. 0.5250 gram substance gave 0.0014 gram ash = 0.27 per cent.

VIII. 0.5737 gram substance gave 0.0013 gram ash = 0.23 per cent.

Percentage Composition of the Ash-free Substance.

							Average.
C	55.12	55.07	..	..	..	..	55.10
H	7.21	7.26	..	..	..	..	7.23
N	..	..	16.26	16.37	..	..	16.31
S	..	..	..	..	0.62	0.64	0.63
O	..	..	..	..	..	..	20.93
							100.00

Preparation D.

3.0 kilos. of freshly ground corn were extracted directly with about 4 litres of 75-per cent. alcohol for 24 hours, at a temperature varying between 40° and 60° C., and filtered while warm. The clear extract was then concentrated to about 500 cc. and the

proteid precipitated by pouring the solution into a large volume of water. The substance so separated, in the form of lumps and strings, was washed frequently with a large amount of water, and finally soaked in water for some hours. It was then collected on muslin, squeezed dry, treated with 95-per cent. alcohol, in which it dissolved readily and almost completely, and again precipitated by water. This process of solution in dilute alcohol and reprecipitation with water was repeated several times, the product ultimately being divided into two fractions, which differed from each other simply in the number of times this process had been repeated. The two products, D^1 and D^2, were then treated repeatedly with absolute alcohol and ether, until all coloring matter and fat had been removed, after which they were ground to a fine powder and portions dried at 110° C. for analysis.

The residue of meal, extracted a second time with warm dilute alcohol, yielded a second portion of zein, which was separated and purified in essentially the same manner as the preceding preparation, the final product being wholly soluble in dilute alcohol. This was likewise reduced to a powder, after successive treatment with ether and absolute alcohol, and a portion dried at 110° C. for analysis. (Product D^2.)

Analysis of Zein. Preparation D^1.

I. 0.3028 gram substance gave 0.1991 gram H_2O = 7.30 per cent. H, and 0.6107 gram CO_2 = 54.99 per cent. C.

II. 0.2455 gram substance gave 0.1590 gram H_2O = 7.20 per cent. H, and 0.4952 gram CO_2 = 55.00 per cent. C.

III. 0.3580 gram substance gave 47.8 cc. N at 16.8° C. and 766.2 mm. pressure = 15.92 per cent. N.

IV. 0.3557 gram substance gave 48.3 cc. N at 18.4° C. and 756.3 mm. pressure = 15.90 per cent. N.

V. 0.5000 gram substance fused with $KOH + KNO_3$ gave 0.0234 gram $BaSO_4$ = 0.64 per cent. S.

VI. 0.5145 gram substance gave 0.0040 gram ash = 0.78 per cent.

Percentage Composition of the Ash-free Substance.

						Average.
C	55.42	55.43	..	..	..	55.42
H	7.35	7.25	..	..	..	7.30
N	..	..	16.04	16.02	..	16.03
S	..	..	..	..	0.64	0.64
O	..	..	..	..	..	20.61
						100.00

Analysis of Zein. Preparation D³.

I. 0.3401 gram substance gave 0.2220 gram H_2O = 7.25 per cent. H, and 0.6857 gram CO_2 = 54.98 per cent. C.

II. 0.3333 gram substance gave 0.2156 gram H_2O = 7.19 per cent. H, and 0.6740 gram CO_2 = 55.14 per cent. C.

III. 0.3696 gram substance gave 50.1 cc. N at 17.0° C. and 757.4 mm. pressure = 15.97 per cent. N.

IV. 0.3731 gram substance gave 50.5 cc. N at 17.9° C. and 755.7 mm. pressure = 15.89 per cent. N.

V. 0.6198 gram substance fused with $KOH + KNO_3$ gave 0.0305 gram $BaSO_4$ = 0.67 per cent. S.

VI. 0.5065 gram substance gave 0.0030 gram ash = 0.59 per cent.

VII. 0.5131 gram substance gave 0.0035 gram ash = 0.68 per cent.

Percentage Composition of the Ash-free Substance.

						Average.
C	55.33	55.49	..	..	..	55.41
H	7.29	7.23	..	..	..	7.26
N	..	..	16.07	15.99	..	16.03
S	..	..	..	..	0.67	0.67
O	..	..	..	..	..	20.63
						100.00

Analysis of Zein. Preparation D³.

I. 0.3638 gram substance gave 0.2366 gram H_2O = 7.22 per cent. H, and 0.7300 gram CO_2 = 54.72 per cent. C.

II. 0.3892 gram substance gave 0.2551 gram H_2O = 7.27 per cent. H, and 0.7846 gram CO_2 = 54.99 per cent. C.

III. 0.4819 gram substance gave 65.3 cc. N at 17.9° C. and 761.2 mm. pressure = 15.99 per cent. N.

IV. 0.4143 gram substance gave 55.6 cc. N at 17.0° C. and 759.7 mm. pressure = 15.86 per cent. N.

V. 0.5200 gram substance gave 0.0038 gram ash = 0.73 per cent.

VI. 0.5163 gram substance gave 0.0039 gram ash = 0.75 per cent.

VII. 1.0117 grams substance fused with $KOH + KNO_3$ gave 0.0395 gram $BaSO_4$ = 0.54 per cent. S.

VIII. 1.0520 grams substance fused with $KOH + KNO_3$ gave 0.0425 gram $BaSO_4$ = 0.56 per cent. S.

Percentage Composition of the Ash-free Substance.

							Average.
C	55.12	55.38	..	..	..	..	55.25
H	7.27	7.32	..	..	..	..	7.29
N	..	..	16.10	15.97	..	..	16.04
S	..	..	..	..	0.54	0.56	0.55
O	..	..	..	..	..	..	20.87
							100.00

A comparison of the analyses of these several preparations of zein, or maize fibrin, shows a remarkable uniformity in composition, and furthermore indicates that the insoluble modification of the proteid is not at all different in composition from the main product. This is plainly apparent from the following table:

	Soluble Zein.						*Insoluble Modification.*			
	A	B	C	D^1	D^2	D^3	A	B	C	Average.
C	55.27	55.20	55.10	55.42	55.41	55.25	54.97	55.37	55.10	55.23
H	7.35	7.29	7.15	7.30	7.26	7.29	7.30	7.19	7.23	7.26
N	16.01	16.20	16.22	16.03	16.03	16.04	16.07	16.29	16.31	16.13
S	0.53	0.55	0.60	0.64	0.67	0.55	0.61	0.63	0.63	0.60
O	20.84	20.76	20.93	20.61	20.63	20 87	21.05	20.52	20.73	20.78
	100.00	100.00	100.00	100.00	100.00	100,00	100.00	100.00	100.00	100.00
Ash	0.24	0.46	0.17	0.78	0.63	0.74	0.19	0.44	0.25	

Maize fibrin, as prepared and analysed by Ritthausen,[1] was found to contain 54.69 per cent. C, 7.51 per cent. H, 16.33 per cent. N and 0.69 per cent. S, thus agreeing very closely with our data, except in carbon. This slight difference in composition obviously cannot be explained with certainty, but considering the great care used in the purification of our products and their close agreement in composition, together with the use of unquestionable analytical methods, it seems probable that the above series of data must accurately represent the true composition of maize fibrin or zein. It is furthermore equally evident from the analytical data that this substance is a homogeneous body, and not composed of two or more dissimilar bodies.

Freshly precipitated zein (precipitated from an alcoholic solution by water) is wholly insoluble in 0.5-per cent. sodium carbonate, even when warmed with the alkaline fluid at 40° C. for 24 hours. It is likewise equally insoluble in 0.2-per cent. hydrochloric acid, but can be completely dissolved by an aqueous solution of potassium hydroxide of 0.2-per cent. strength. So dissolved it is not converted into alkali-albumin, as is indicated by the fact that the precipitate produced on neutralisation of the alkaline fluid is not soluble in excess of dilute acid, but is completely dissolved by alcohol. This resistance of the proteid to the

[1] "Ueber den Stickstoffgehalt der Pflanzen-Eiweisskörper."—Pflüger's Archiv für die gesammte Physiologie **18**, 246.

action of alkalies is quite pronounced; thus, exposure of the substance to the action of 0.2-per cent. caustic potash at 40° C. for 24 hours is not followed by any conversion into alkali-albumin. This is likewise true even when the strength of the alkali is raised to 2.0-per cent. KOH. Exposure to a higher temperature than 40° C. with this strength of alkali is, however, followed by a change in the proteid.

Freshly precipitated zein is wholly insoluble in water, and on being boiled with water is changed into the insoluble modification already referred to, which is insoluble both in alcohol and dilute (0.2-per cent.) potassium hydroxide. Zein gives the usual proteid reactions with Millon's xanthoprotein and biuret tests.

On warming the proteid at 40° C. with pepsin-hydrochloric acid, the substance is gradually dissolved and converted into proteose-like bodies, and true peptones non-precipitable by saturation with ammonium sulphate.

Boiled with dilute sulphuric acid (6 cc. concentrated acid in 300 cc. water) zein at first melts, forming a gummy mass or lump which is only slowly attacked by the acid, the portion dissolved being mainly converted into proteoses and peptone. Heated with stronger sulphuric acid, it undergoes a more pronounced decomposition, yielding large amounts of leucin with considerable tyrosin, and apparently large amounts of glutamic acid.

Corn meal, after thorough extraction with salt-solution and warm dilute alcohol, yields little proteid matter to dilute solutions of potassium hydroxide (0.2-per cent.).

Summary.

1. The maize-kernel contains several distinct proteids, well characterised in reactions and composition. Of these, there are three globulins, one or more albumins, and an alcohol-soluble proteid.

2. The globulin obtainable from the maize-kernel by extraction with 10-per cent. solution of sodium chloride and separation by the usual methods—as by dialysis, or by precipitation with ammonium sulphate, followed by dialysis—is a mixture of two or more dissimilar globulins, differing from each other both in composition and in coagulation-points.

3. The mixed globulin can be approximately separated into its

two constituents by fractional heat-coagulation, or by a process of "recrystallisation" from warm dilute salt-solution. In the former process, there is at the same time formed a small amount of proteose-like bodies, presumably by hydrolysis of the less resistant globulin.

4. The two globulins separable by the above methods from the mixed globulin are a myosin-like body and a vitellin-like body.

The myosin-like globulin is characterised by containing about 16.8 per cent. of nitrogen and 1.2 per cent. of sulphur, agreeing closely in its composition with animal myosin. It has, however, a coagulation-point (in 10-per cent. salt solution) of about 70° C.

The vitellin-like globulin, on the other hand, contains about 18.1 per cent. of nitrogen and 0.85 per cent. of sulphur, agreeing closely with the generally accepted composition of phyto-vitellin. This body, however, is almost entirely non-coagulable by heat when dissolved in dilute salt-solution, except in the presence of acetic acid. It is more soluble in warm salt-solutions than in cold, and when separated from the former by cooling the fluid, or on dialysis, almost invariably appears in the form of small spheroids.

5. These two globulins exist as such in the corn or maize kernel, and are not products of a cleavage of the so-called mixed globulin. This is evident from the coagulation-points of a salt-solution of the mixed globulin; from the fact that the separation can be accomplished without the aid of heat; and, lastly, since it is possible to directly extract the individual globulins from the kernel, by the use of appropriate solvents.

6. Direct extraction of finely powdered corn meal with water yields a dilute salt-solution, which dissolves the myosin-like globulin, leaving the bulk of the vitellin-like substance undissolved. Probably, the character of the salts present in the kernel plays an important part in this separation. From this solution the myosin can be separated in a fair degree of purity by the usual methods.

7. Extraction of corn meal with 10-per cent. salt solution, after previous extraction with water, dissolves the vitellin-like globulin, from which solution it can be separated by the customary methods. So prepared, it agrees exactly with the vitellin separated by heat-coagulation from the mixed globulin.

8. The third globulin present in the maize-kernel is characterised by extreme solubility in very dilute salt-solutions, especially phosphates and sulphates. It separates from such solutions only

by prolonged dialysis—*i. e.* not until nearly every trace of the above salts has been removed. It coagulates (in a 10-per cent. salt solution) in the neighborhood of 62° C., and contains 15.2 per cent. of nitrogen and 1.26 per cent. of sulphur.

9. Through the long-continued action of water, and also of strong solutions of salt, as ammonium sulphate, the myosin-like globulin, and the globulin with a still lower content of nitrogen, are changed into insoluble modifications, soluble, however, in 0.5-per cent. sodium carbonate solution, from which they are precipitated on neutralisation, apparently as albuminates. So prepared, these insoluble modifications are characterised by a relatively high content of carbon.

10. An aqueous extract of corn meal, as well as a sodium-chloride extract, contains, in addition to the globulins, apparently two albumin-like bodies, more or less coagulable by heat, but as prepared, unlike in chemical composition.

11. A certain amount of proteose can be detected in the extracts of corn meal, after the globulins and albumins have been entirely removed, but apparently this is mainly, if not wholly, an artificial product resulting from the hydrolysis of some one or more of the preceding bodies.

12. Especially noteworthy is the presence in the maize-kernel of a peculiar proteid body known as maize fibrin, or better as *zein*, soluble in warm dilute alcohol, but insoluble in water.

Zein is characterised by a high content of carbon, by its resistance to the action of dilute alkalies (*i. e.*, non-convertibility into alkali-albuminate), and by the ease with which it is converted into an insoluble modification on being warmed with water, or with very weak alcohol.

Soluble zein and the insoluble modification have the same chemical composition. Both respond to the ordinary proteid reactions.

Contributions from the Chemical Laboratory of Cornell University.

DECOMPOSITION WITH ALCOHOL OF THE DIAZO COMPOUNDS OBTAINED FROM SOME OF THE NITRO-NAPHTHYL-AMINES.

By W. R. Orndorff and M. Cauffman.

In a previous paper[1] it was shown that when the α-diazo-naphthalene sulphate is decomposed by alcohol, about 40 per cent. is converted into naphthalene and 23 per cent. into the ethyl ether of α-naphthol. With the β-diazo-naphthalene salts, however, it was found that, when decomposed by alcohol in exactly the same manner, about 30 per cent. was converted into the ethyl ether of β-naphthol, and only 7 per cent. was obtained in the form of naphthalene. From these results it was concluded that in the case of the simple diazo-naphthalene salts, when decomposed by alcohol, the course of the reaction is influenced by the position of the diazo group in the naphthalene molecule. When the diazo group occupies the α-position the tendency is toward the introduction of hydrogen according to the well known equation:

$$C_{10}H_7.N_2.HSO_4 + C_2H_6O = C_{10}H_8 + C_2H_4O + N_2 + H_2SO_4.$$

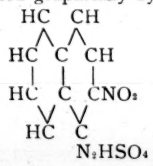
When, however, the diazo group is removed to the β-position the reaction proceeds in a different manner; the tendency here is towards the introduction of the ethoxy group in place of the diazo group as shown in the equation:

$$C_{10}H_7.N_2.HSO_4 + HO.C_2H_5 = C_{10}H_7OC_2H_5 + N_2 + H_2SO_4.$$

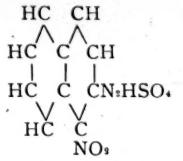
Remsen and his pupils have shown that in the case of the substituted diazo-benzene salts, not only the position of the diazo group in the molecule with reference to other groups, but the character of the substituting group or atoms exerts an influence on the course of the reaction, when these compounds are decomposed by alcohol. Thus while the diazo-benzene salts themselves, when decomposed by alcohol, were found to yield principally phenol ethers, the nitro-diazo-benzene salts made from the ortho-, meta- and para-nitranilines gave only nitro-benzene. The influence of the nitro group on the course of the reaction is plainly shown here. The diazo group is replaced by hydrogen in each case, and it seems to make no difference whether the nitro group occupies the ortho, meta, or para position with reference to the diazo group.

[1] This Journal **13**, 153.

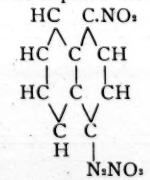
The study of the decomposition by alcohol of the nitro-diazo-naphthalene salts obtained from the nitro-naphthyl-amines was undertaken in order to determine if the influence of the nitro group was the same in the naphthalene as in the benzene series. Moreover, it is possible in the naphthalene series to obtain two compounds, in which the position of the nitro group with reference to the diazo group does not change, although the diazo group is first in the α-, and then in the β-position. Thus β_2-nitro-α_2-diazo-naphthalene sulphate, represented graphically by the following formula,



may be readily made, and also α_2-nitro-β_2-diazo-naphthalene sulphate,



In these two subtances it will be seen, that though in the first case the diazo group is in the α-position, and in the second in the β-, the nitro group in both cases is in the ortho position with reference to the diazo group. By decomposing these two compounds with alcohol it was hoped the influence of the nitro group could be determined irrespective of the position it occupied in the molecule with reference to the diazo group. Incidentally the decomposition of α_1-nitro-α_2-diazo-naphthalene nitrate,



by alcohol was studied for the sake of completeness, and in order to show the influence, if any, of the position of the nitro group on the course of the reaction. In designating the position of the groups in the naphthalene molecule, reference is made to the formula on page 134, volume II., of Beilstein's "Handbuch der organischen Chemie."

Preparation of the $\beta_2\alpha_2$-nitro-naphthyl-amine and of the $\alpha_1\alpha_2$-nitro-naphthyl-amine.—The $\beta_2\alpha_2$-nitro-naphthyl-amine and the $\alpha_1\alpha_2$-nitro-naphthyl-amine were made together. For this purpose α-naphthyl-amine was converted into the acet-naphthalide according to the directions of Liebermann,[1] and the acet-compound purified by recrystallisation from hot water. The product obtained was pure and melted at 159°. The $\beta_2\alpha_2$- and the $\alpha_1\alpha_2$-nitro-acet-naphthalide were then made by dissolving the acet-compound in glacial acetic acid, adding fuming nitric acid and allowing the mixture to stand. The two products crystallised out together. These were filtered off, and from the mother-liquor on standing, some of the pure $\alpha_1\alpha_2$-nitro-acet-naphthalide afterwards crystallised out. Since the two nitro compounds crystallised out together and gave a product melting at 171°, which it was impossible to separate into its constituents by fractional crystallisation, the method recommended by Lellmann and Remy[2] was tried. The double compound was treated with about sixty per cent. of the theoretical amount of caustic potash necessary to saponify. The $\alpha_1\alpha_2$-product under these conditions is saponified, the $\beta_2\alpha_2$-nitro-acet-naphthalide remaining unchanged. The $\alpha_1\alpha_2$-nitro-naphthyl-amine was separated from the $\beta_2\alpha_2$-nitro-acet-naphthalide by the second method recommended by Lellmann and Remy[2], and both substances were purified by recrystallisation from alcohol. The $\beta_2\alpha_2$-nitro-acet-naphthalide was then saponified in alcoholic solution with concentrated hydrochloric acid, and the product recrystallised from alcohol. The $\beta_2\alpha_2$-nitro-naphthyl-amine melted at 144°, while the $\alpha_1\alpha_2$-product melted at 191°.

Preparation of the β_2-nitro-α_2-diazo-naphthalene sulphate.—The $\beta_2\alpha_2$-nitro-naphthyl-amine was dissolved in a small amount of ordinary alcohol, an excess of concentrated sulphuric acid gradually added, and, after cooling, a little more than the theoretical amount of amyl nitrite was added. The diazo compound was then crystallised out of the solution by the addition of ether, and

[1] Ann. Chem. (Liebig) **183**, 229. [2] Ber. d. chem. Ges. **20**, 892.

cooling in a freezing-mixture. The diazo sulphate was then filtered off, and on the addition of more ether to the filtrate and cooling, a further crop of crystals of the diazo sulphate was obtained.

Several attempts were made to obtain the nitro-diazo-naphthalene nitrate, but without success, and as the supply of the $\beta_2\alpha_2$-nitro-naphthyl-amine was small, the attempt was abandoned.

The β_2-nitro-α_2-diazo-naphthalene sulphate was washed with absolute alcohol and dry ether, carefully dried in the dark under sulphuric acid, and subjected to an analysis. For this purpose the diazo salt was decomposed in the usual way in water, the nitrogen evolved, collected and measured, and the acid titrated with a standard alkali solution. The following results were obtained:

I. 0.0587 gram gave 4.9 cc. nitrogen at 23° and 742 mm. bar.
I. 0.0587 gram gave 0.01566 gram sulphur trioxide.
II. 0.0905 gram gave 7.8 cc. nitrogen at 23° and 742 mm. bar.
II. 0.0905 gram gave 0.0246 gram sulphur trioxide.

	Calculated for $C_{10}H_6{<}^{NO_2}_{N_2HSO_4}$.	Found. I.	II.
N_2	9.42	9.19	9.47
SO_3	26.93	26.68	27.18

Properties of the β_2-nitro-α_2-diazo-naphthalene sulphate.—The β_2-nitro-α_2-diazo-naphthalene sulphate thus prepared crystallises in yellow needles, which are insoluble in ether and absolute alcohol, but soluble in water and dilute alcohol. When heated with water, decomposition takes place, nitrogen is evolved, and β_2-nitro-α_2-naphthol results. Heated alone it explodes feebly, but does not decompose on percussion. The salt decomposes when left exposed to the light and air, the crystals becoming finally red in color. An examination of the crystals was kindly made by Professor Kemp, formerly of the Geological Department of Cornell University, and now of Columbia College, who reported as follows: "The felty substance is shown under the microscope to consist of a mass of small acicular crystals of a strong lemon-yellow color. They average about one-fortieth of a millimeter in diameter and are several times as long. They seem to have an hexagonal cross-section and to form slender hexagonal prisms. No terminations could be detected, as their ends were broken. Pleochroism is present, yellow to lighter yellow; the lighter tint appearing in

the ray vibrating parallel to the long axis of the prism. With crossed nicols the needles extinguish, in some cases parallel, in others at about 7° to 10°, and in others from 18° to 25°. This variation doubtless corresponded to the different portions that were uppermost. They indicate that the crystals are either monoclinic or triclinic. The parallel extinction makes the probability of their being monoclinic greater than triclinic, although the possibility of an inclined extinction of the latter being very near parallelism cannot be overlooked. They polarise in brilliant colors, and have a quite high refractive index. On exposure to the air the color of the needles changes in a few days to an orange tint, and then to an opaque brick-red."

Decomposition of the β2-nitro-α1-diazo-naphthalene sulphate in alcohol.—The method given by Lellmann[1] was made use of, and the diazo compound was not isolated. The β2α1-nitro-naphthylamine was dissolved in just enough alcohol to prevent its precipitating out on cooling, an excess of concentrated sulphuric acid was added, the mixture cooled, and a large excess of ethyl nitrite in alcohol added. As long as the mixture was kept cool, no change took place, but as soon as it acquired the temperature of the room, nitrogen was given off freely, and the odor of aldehyde was quite marked. The reaction was completed by warming on the water-bath. Water was added to the red-colored fluid while hot and a substance crystallised out. This was allowed to settle, and was then filtered off, and the filtrate examined, but was found to contain nothing but sulphuric acid and some tar. The precipitate was then dissolved in dilute alcohol and recrystallised fractionally, and the melting-point of each fraction determined in order to detect the presence of a second substance. The melting-point, however, remained constant at about 76°–79°, the variation being due to the presence of a small amount of tarry matter. The crystals, besides showing the same melting-point as β-nitro-naphthalene, exhibited the same solubility in alcohol and the same crystal form under the microscope, and on analysis gave the following results:

0.5028 gram gave 0.0495 gram ammonia by the modified Kjeldahl method.

	Calculated for $C_{10}H_7NO_2$.	Found.
N	8.9 per cent.	8.10 per cent.

[1] Ber. d. chem. Ges. **19**, 236.

The other substance which we would naturally expect to get here, would be the ethyl ether of β_2-nitro-α_2-naphthol. This is not known, but as the β_2-nitro-α_2-naphthol itself melts at 128°, it seems fair to suppose that the presence of even a small quantity of the ethyl ether of β_2-nitro-α_2-naphthol would have shown itself by raising the melting-point of the crystals. The only change noted, however, was a slight *lowering* of the melting-point, and this was probably due to the presence of a small amount of tar. The only product of the decomposition of β_2-nitro-α_2-diazo-naphthalene sulphate in alcohol, therefore, is β-nitro-naphthalene. *The hydrogen reaction alone takes place in this case.* From 4.17 grams of the β_2-nitro-α_2-naphthyl-amine taken, 3.23 grams of β-nitro-naphthalene were obtained, which corresponds to a conversion of about 84 per cent. of the diazo compound into β-nitro-naphthalene. Attention should be called here to the fact that when α-diazo-naphthalene sulphate itself was decomposed in alcohol, 40 per cent. was converted into naphthalene, and 23 per cent. into the ethyl ether of α-naphthol.

Preparation of the α_2-nitro-β_2-naphthylamine.—The directions of Liebermann and Jacobson,[1] slightly modified by Merz and Weith,[2] were followed closely in the preparation of this substance. β-Naphthylamine was heated with glacial acetic acid, and thus converted into the acet-compound, which was recrystallised from alcohol. The nitro group was then introduced by dissolving the acet-compound in glacial acetic acid and adding fuming nitric acid. This, when recrystallised from alcohol, was found to have the melting-point 123°. The α_2-nitro-β_2-acet compound was then saponified in alcoholic solution with caustic potash, and the nitro-naphthyl-amine precipitated by adding water. On recrystallising from alcohol the crystals were found to melt sharply at 126°–127°.

Preparation of the α_2-nitro-β_2-diazo-naphthalene sulphate.—The method pursued in preparing the α_2-nitro-β_2-diazo-naphthalene sulphate was the same that was used in the preparation of the β_2-nitro-α_2-diazo-naphthalene sulphate. The nitro-naphthyl-amine was dissolved in sufficient hot alcohol to prevent its precipitating out on cooling; an excess of concentrated sulphuric acid was gradually added to the well-cooled solution, and then, keeping the solution in ice water, a little more than the theoretical amount of amyl nitrite was added. The color of the solution changed from light to dark red, and on adding ether and cooling in a freezing-

[1] Ann. Chem. (Liebig) **211**, 45. [2] Ber. d. chem. Ges. **14**, 2343.

mixture, the α_2-nitro-β_2-diazo-naphthalene sulphate crystallised out after standing a short time. The mother-liquor was then treated with more ether, again cooled in a freezing-mixture, when more of the diazo compound crystallised out.

From 15 grams of the α_2-nitro-β_2-naphthyl-amine about 17 grams of the diazo compound were obtained, which is about 72 per cent. of the theoretical amount. The diazo salt was then washed with absolute alcohol and ether, dried in the dark, and analysed by decomposing in water, collecting and measuring the nitrogen evolved and titrating the sulphuric acid with a standard alkali solution. The following results were obtained:

In the determination of nitrogen—

I. 0.0811 gram gave 6.4 cc. nitrogen at 21° and 747 mm. bar.

II. 0.0545 gram gave 4.5 cc. nitrogen at 22° and 746 mm. bar.

For sulphuric acid—

I. 0.8811 gram gave 0.02186 gram sulphur trioxide.

II. 0.0545 gram gave 0.01493 gram sulphur trioxide.

	Calculated for $C_{10}H_6\langle^{NO_2}_{N_2HSO_4}$	Found. I.	II.
N_2	9.42 per cent.	8.82	9.17
SO_3	26.93 "	26.95	27.39

Properties of α_2-nitro-β_2-diazo-naphthalene sulphate.—The α_2-nitro-β_2-diazo-naphthalene sulphate crystallises in orange-yellow needles which, though readily soluble in water and dilute alcohol, are difficultly soluble in absolute alcohol and insoluble in anhydrous ether. When heated with water, nitrogen is evolved and α_2-nitro-β_2-naphthol results; when heated alone, the substance explodes feebly at 167° but does not explode on percussion. The diazo salt undergoes decomposition when left exposed to the light and air, the color finally becoming brown. When protected from the action of the light, the crystals lost their color very slowly, and a change was barely perceptible after the lapse of several days.

Decomposition of the α_2-nitro-β_2-diazo-naphthalene sulphate in alcohol.—The α_2-nitro-β_2-diazo-naphthalene sulphate was decomposed in absolute alcohol according to the method already described.[1] The odor of aldehyde was perceptible throughout the experiment. The contents of the flask were then filtered to remove a small amount of tar, and the excess of alcohol distilled

[1] This Journal **13**, 156.

off on the water-bath. This alcoholic distillate smelled strongly of aldehyde. A large quantity of water was then added to the flask and the whole subjected to distillation in steam. A light yellow substance distilled with the steam. When the solid ceased to distil with the steam, the operation was discontinued, and the non-volatile residue remaining in the flask was examined.

The residue.—This consisted of water containing sulphuric acid and a tarry substance. The tar was filtered off, the acid neutralised, and the solution slowly evaporated, but besides the sulphate and a small amount of tar, nothing else was detected. The tar was now dissolved in alcohol and the solution divided into two portions, one of which was precipitated with water, adding a little at a time and allowing to settle and then filtering; the second was decolorised by boiling with bone-black and allowed to evaporate spontaneously. From the first solution a few crystals were obtained, melting at 58° and possessing other properties which proved them to be α-nitro-naphthalene. From the second only tarry matter could be separated.

The distillate.—The contents of the receiver were allowed to settle over night, then filtered and the precipitate dried. This precipitate was then dissolved in alcohol and subjected to fractional crystallisation. The melting-point of the various fractions remained constant at about 58°. Only the last portions varied one or two degrees from this point, melting at 56°, and this was shown to be due to traces of tar present in the crystals. The crystals melted at 58°, the melting-point of α-nitro-naphthalene, possessed the same solubility in alcohol, and same crystal form under the microscope. On reduction with iron and acetic acid they gave α-naphthyl-amine, characterised by its peculiar and unpleasant odor, and melting-point of 50°. A determination of the nitrogen in the nitro product by the modified Kjeldahl method gave the following results:

0.7041 gram gave 0.0709 gram ammonia.

	Calculated for $C_{10}H_7NO_2$.	Found.
N	8.09	8.28

The substance is undoubtedly α-nitro-naphthalene. The ethyl ether of α_2-nitro-β_2-naphthol, which we would expect here as one of the products of the decomposition of the diazo compound in alcohol, melts at 103°–104°, and if any of this substance had been

present the melting-point would not have remained constant. The only product therefore of the decomposition of the α_2-nitro-β_2-diazo-naphthalene sulphate in alcohol is α-nitro-naphthalene. *The hydrogen reaction alone takes place here.* From 8.1 grams of the diazo compound 2.45 grams of the nitro-naphthalene were obtained, which corresponds to a conversion of about 52 per cent. of the diazo compound into α-nitro-naphthalene. It should be remembered in this connection that when β-diazo-naphthalene sulphate itself was decomposed in alcohol, 30 per cent. was converted into the ethyl ether of β-naphthol and only 7 per cent. into naphthalene.

Preparation of the α_2-nitro-β_2-diazo-naphthalene nitrate.—The α_2-nitro-β_2-naphthyl-amine was dissolved in a small quantity of alcohol, the solution cooled, and then an excess of concentrated nitric acid gradually added. The nitrate thus prepared was diazotised by cooling the solution and adding gradually a little more than the theoretical amount of amyl nitrite. The solution turned dark-red and gave yellow crystals of the α_2-nitro-β_2-diazo-naphthalene nitrate on adding ether and cooling. An analysis of the diazo nitrate by the usual method gave the following results:

0.0365 gram gave 3.6 cc. nitrogen at 21° and 742 mm. bar.

0.0365 gram gave 0.0085 gram NO_2.

	Calculated for $C_{10}H_6{<}^{NO_2}_{N_2.NO_3}$	Found.
N_2	10.68	10.97
NO_2	23.66	23.28

Properties of the α_2-nitro-β_2-diazo-nitrate.—The diazo salt is soluble in water and dilute alcohol, insoluble in ether which is free from water. It crystallises in light-yellow colored needles which rapidly turn dark brown when exposed to the light. It explodes on heating, but not by percussion. The decomposition with water and alcohol gave the same products that were obtained with the diazo sulphate.

Preparation of α_1-nitro-α_2-diazo-naphthalene nitrate.—The α_1-nitro-α_2-diazo-naphthalene nitrate was made by adding just enough absolute alcohol to the α_1-nitro-α_2-naphthyl-amine to form a thin paste; this was then treated with an excess of dilute nitric acid, and a little more than the theoretical amount of amyl nitrite slowly added until everything went into solution. The diazo compound was then precipitated out with ether in the cold.

Several other methods were tried, but this one yielded the most satisfactory results. Many attempts were made to obtain the diazo sulphate, but without success. In all cases the sulphate failed to crystallise out, and a red dye-stuff, which turned blue on treatment with sulphuric acid, was obtained instead. This dye-stuff corresponds to the diazo-amido compound, $C_{20}H_{13}N_5O_4$, obtained by Liebermann[1] under similar circumstances from α_1-nitro-α_2-naphthylamine.

The yellow needles of the diazo nitrate were filtered off, washed as usual with absolute alcohol and anhydrous ether, and dried in the dark. An analysis gave the following results:

In the determination of nitrogen—

I. 0.0327 gram gave 3.1 cc. nitrogen at 23° and 742 mm. bar.

II. 0.2320 gram gave 21.4 cc. nitrogen at 22° and 740 mm. bar.

For nitric acid—

0.2320 gram gave 0.0539 gram NO_3.

	Calculated for $C_{10}H_6<\begin{matrix}NO_3\\N_2NO_3\end{matrix}$.	Found. I.	II.
N_2	10.68	10.37	10.16
NO_3	23.66	...	23.23

Properties of α_1-nitro-α_2-diazo-naphthalenenitrate.—The α_1-nitro-α_2-diazo-naphthalene nitrate crystallises in light-yellow colored needles, which turn to a greenish yellow on short exposure to the light. It is readily soluble in water, moderately so in alcohol, and insoluble in anhydrous ether. It explodes feebly on ignition but not by percussion. Under the microscope the crystals appear as prisms of a deep yellow color.

Decomposition of the α_1-nitro-α_2-diazo-naphthalene nitrate in alcohol.—The method of Liebermann[2] was followed here, and the diazo compound was not isolated. Nitrogen trioxide, generated in the usual way from arsenic trioxide and nitric acid, was conducted into a well-cooled pasty mixture of α_1-nitro-α_2-naphthylamine and dilute nitric acid until all the amido compound had gone into solution. The solution was then filtered, a large quantity of alcohol added, and the whole boiled in a flask provided with a reflux condenser until the nitrogen ceased to be given off. The alcohol was then distilled off on the water-bath and was found to smell strongly of aldehyde. Water was now added to the flask, when a heavy oil separated out, which was allowed to settle for a

[1] Ann. Chem. (Liebig) **183**, 234. [2] Ibid. **183**, 234.

day or two and then distilled in steam until nothing but water passed over.

The residue.—The non-volatile residue left in the flask consisted of a tarry mass which was filtered off and treated with alcohol. A portion dissolved, coloring the solution deep red, but from the solution no crystals could be obtained by concentrating. The filtrate was neutralised with an alkali and also evaporated to crystallisation, but nothing but the nitrate could be isolated.

The distillate.—The contents of the receiver were allowed to settle and then filtered, the precipitate dried and dissolved in alcohol. This alcoholic solution was then subjected to fractional crystallisation. The melting-point of the different fractions, however, remained constant at about 56° to 58° even to the very last portion. From the agreement of the melting-point and solubility in alcohol and crystalline form, it was concluded we had here to deal with the α-nitro-naphthalene. A small quantity of the substance was reduced with iron and acetic acid, when the well known α-naphthyl-amine was obtained. A determination of the nitrogen in the nitro compound by the modified Kjeldahl method gave the following results:

0.5420 gram gave 0.0535 gram ammonia.

	Calculated for $C_{10}H_7NO_2$.	Found.
N	8.09 per cent.	8.12 per cent.

Again, the only product of the decomposition of the diazo compound in alcohol is the nitro-naphthalene. *The hydrogen reaction alone takes place.*

From 4.8 grams of the α_1-nitro-α_2-naphthyl-amine, 2.53 grams of α-nitro-naphthalene were obtained, which corresponds to a conversion of about 57 per cent. of the diazo compound into α-nitro-naphthalene.

Summary.

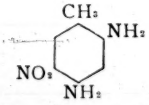
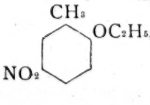
The results of this work may be summed up as follows:

The β_2-nitro-α_2-diazo-naphthalene sulphate, when decomposed in alcohol, gives only β-nitro-naphthalene. The yield of the nitro-naphthalene is very good, corresponding to a conversion of about 84 per cent. of the diazo compound used.

The α_2-nitro-β_2-diazo-naphthalene sulphate gives only α-nitro-naphthalene when decomposed in the same manner with alcohol. The yield here was not so good, corresponding to a conversion of

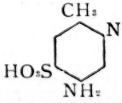
only about 52 per cent. of the diazo compound in this way. The α_1-nitro-α_2-diazo-naphthalene nitrate also gives only α-nitro-naphthalene when decomposed in alcohol. Here, too, the yield was not large, corresponding to a conversion of about 57 per cent. of the diazo compound.

From these results it will be seen that in the case of the diazo compounds obtained from these nitro-naphthyl-amines, the hydrogen reaction alone prevails when these compounds are decomposed in alcohol. Similar results were obtained by Remsen and Graham[1] in the decomposition of the diazo compounds made from the ortho-, meta- and para-nitraniline. In these cases also the hydrogen reaction alone took place. The influence of the nitro group is the same, therefore, both in the benzene and the naphthalene compounds, and the position of the nitro group with reference to the diazo group seems to have no influence on the reaction, the hydrogen reaction taking place in all cases.

It is a matter of interest to note that among all the substituted diazo compounds which give the ethoxy group in place of the diazo group when decomposed by alcohol, only two compounds containing the nitro group have been recorded. One of these is the diazo compound obtained from nitro-toluylene-diamine,[2] $C_6H_2\begin{cases}CH_3(1)\\NH_2(2)\\NH_2(4)\\NO_2(5)\end{cases}$. On treating an alcoholic solution of this substance with nitrogen trioxide and boiling, the ethyl ether of nitro-cresol was obtained having the formula $C_6H_2\begin{cases}CH_3(1)\\OC_2H_5(2)\\NO_2(5)\end{cases}$. In other words  gave  . Here one of the diazo groups, ortho to the nitro group, was replaced by hydrogen, plainly showing the influence of the nitro group on the course of the reaction; while the other diazo group, para to the nitro group *but ortho to the methyl group*, was substituted by the ethoxy group. It has already been shown in a previous paper[3]

[1] This Journal **11**, 319. [2] Ber. d. chem. Ges. **7**, 1212; Ann. Chem. (Liebig) **217**, 155.
[3] This Journal **9**, 337.

that the methyl group in the *ortho* position brought about the ethoxy reaction alone, and in the para position the hydrogen reaction; and it will be seen that the influence of the ortho methyl group is stronger here even than that of the para-nitro group to induce the hydrogen reaction. It must be noted, however, that the influence both of the nitro group and of the methyl group was in the same direction in the case of the diazo group which was replaced by hydrogen, and in opposite directions in the other case.

The other compound is one mentioned by Limprich,[1] and also by von Pechmann.[2] It is nitro-toluidine sulphonic acid, having the structure represented by the formula  When the diazo compound obtained from this substance was decomposed by sodium and alcohol it gave the ethoxy compound. When decomposed in a sealed tube with alcohol alone at 100°, however, it gave only nitro-toluene-sulphonic acid, as we would naturally expect, so that it appears that the sodium here exercises some influence, and this case can hardly be cited as an exception to the general rule that the tendency of the nitro group when present in the molecule of a diazo compound, is to induce the hydrogen reaction when the compound is decomposed in alcohol. A very large number of cases might be mentioned in proof of this statement, and only one exception, viz. nitro-toluylene-diamine.

CORNELL UNIVERSITY, *Nov.* 25, 1891.

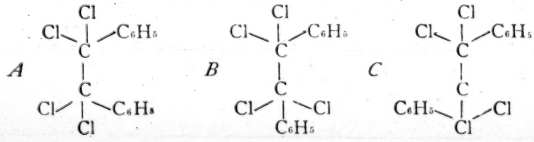
[1] Ber. d. chem. Ges. **18**, 2185. [2] Ann. Chem. (Liebig) **173**, 215.

REVIEWS AND REPORTS.

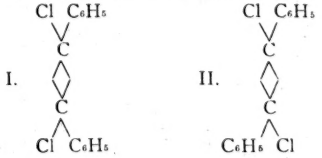
STEREOCHEMISTRY.

(*Continued from* p. 588, *Vol.* 13.)

Already the general theory of Wislicenus has received the support of quantitative experiments. For example, the formula of tolane tetrachloride has three configurations (*A*, *B*, *C*), in which chlorine atoms occupy "corresponding" positions:



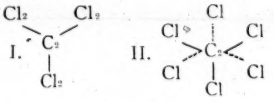
If two atoms of chlorine be removed by a reducing agent, as zinc, the removal will presumably take place only when these chlorine atoms are in corresponding positions; hence only the three configurations given need be taken into account; of these *A* only can yield the unstable dichloride I, while both the other configurations will yield the stable dichloride II:



At a temperature high enough to cause incessant relative rotation of the upper and lower halves of all the tetrachloride molecules, there will be then, for every molecule in a position to yield the unstable, two molecules in a position to yield the stable dichloride. Accordingly experiment showed that at 80° C. one-third of the reduction-yield consisted of the unstable and two-thirds of the stable isomer.[1] As the temperature falls the directive affinities regain the upper hand; in centers of heat-disturbance rotation continues and produces the unfavored configuration *A* as before, but in other parts of the mass the favored configurations *B* and *C* occur alone; accordingly, if the reduction is carried out at 20° C. considerably more than two-thirds of the yield consists of the stable dichloride.

[1] Blank: Ann. Chem. (Liebig) **248**, 27; and comp. This Journal **12**, 231.

These results also throw light on the much-discussed problem as to the circumstances in which relative rotation of singly-linked carbon atoms occurs, and as to the number of isomers resulting. The results show the rotation to depend on the temperature much as dissociation does; and they show the existence of two isomers, the rotating and the non-rotating, of which the former yields on reduction both dichlorides, the latter the stable dichloride only. For some substances the temperature of regular rotation may lie below the ordinary temperature. According to Wislicenus[1] this must be the case when the six radicles attached to the two carbon atoms are all alike; then there will be "free rotation," *i. e.*, rotation practically free from resistance, caused therefore by the slightest heat-disturbance—any temperature above absolute zero. Auwers and Meyer[2] have again brought forward this view and maintain that otherwise there would be two formulæ for a substance like perchlorethane representing two different forms of the substance equally stable:



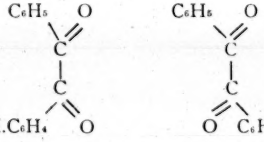
These formulæ are supposed to be viewed from above; in I the lower chlorine atoms are directly under, in II half way between the others. Since in reality there is only one compound of the formula C_2Cl_6, we must assume, it is said, perpetual relative rotation of the upper and lower chlorine groups. It has been objected[3] that if chlorine be supposed to repel chlorine, the only permissible formula is the second. If, on the other hand, we prefer to assume that chlorine attracts chlorine, only the first configuration will be stable. In either case the necessity for the assumption of free rotation disappears.

Bethmann[4] approached this subject from quite a different side. He determined the affinity-constant of various organic acids by measuring their electric conductivity. In the case of succinic acid, he concluded that no relative rotation of the central carbon atoms takes place "because all the samples of the acid examined gave the same constant." This very fact that all samples of succinic acid have the same properties, *i. e.* that there is only one succinic acid, had been used by Victor Meyer to show that in it rotation is perpetual. In reality the fact proves only that one or other of these views is correct:[5] either no position is of

[1] Räumliche Anordnung, p. 14.
[2] Ber. d. chem. Ges. **23**, 2082. It is here stated that according to Wislicenus the rotation will be free when the six radicles are not alike. But see the passage in the "Räumliche Anordnung" just cited.
[3] J. prakt. Chem. (2) **43**, 124. Comp. Bischoff: Ber. d. chem. Ges. **24**, 1093.
[4] Ztschr. phys. Chem. **5**, 385.
[5] Comp. Warder: Am. Ass. Adv. Sci. **39**, 111.

superior stability, or one position is so far superior that no other can compete with it. However, other facts observed by Bethmann are, as will be seen, so easily explained by supposing the relative positions of the radicles composing succinic acid to be permanent in the absence of disturbing influences, that V. Meyer now accepts this view. Baeyer explains some of his results (see *post*) on the same assumption, which is in accord also with the opinions of Van't Hoff and Wislicenus. On the other side stands Bischoff,[1] as we shall see; apparently alone.

Where no one position of the six peripheral radicles is pre-eminently stable, there may, it has been said, be two or more positions of equilibrium; in this case there will be observed among ethane derivatives an isomerism analogous to that at present known only among ethylene derivatives. The two mono-carboxyl ortho-derivatives of benzil may prove to be an instance of such isomerism (Graebe[2]):



In the meantime the simple statement of Van't Hoff stands unshaken: "If the mutual action [of the indirectly connected radicles] depends, as every known force does, on the distance and the nature of the radicles in question, there will be among the possible positions only one which corresponds to the state of stability" (l. c., p. 52).

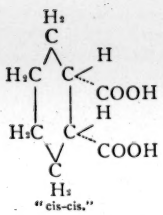
The Mutual Affinity of Indirectly Connected Radicles—(Baeyer).

Wislicenus had assumed that the greater the difference in the positivity of two radicles in a molecule not directly connected with each other, the greater would be their mutual attraction. Baeyer[3] suggests as a "slight modification" that the attraction corresponds to that which would exist between the two radicles if they were directly connected. Baeyer's objection to the assumption of Wislicenus is based on the properties of the two symmetrical dimethyl-succinic acids, and on the relation between these acids and the two hexa-hydrophthalic acids:

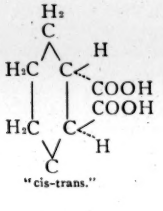
[1] Ber. d. chem. Ges. **23**, 1958.

[2] Ber. d. chem. Ges. **23**, 1344. The suggestion that the benziloximes are a case in point has been withdrawn by its authors (Auwers and Meyer: Ber. d. chem. Ges. **23**, 2402).

[3] Ann. Chem. (Liebig) **258**, 185.

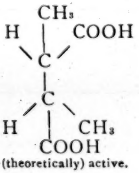


"cis-cis."



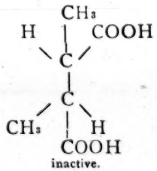
"cis-trans."

The most favored positions for the methyl-succinic acids are, according to Wislicenus,



(theoretically) active.

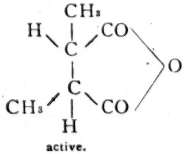
and



inactive.

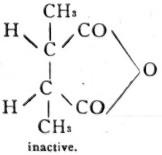
These formulæ do not show why the inactive acid forms an anhydride more readily than the active acid.

Again, the formulæ for the anhydrides would be



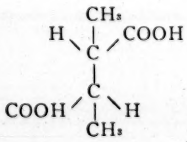
active.

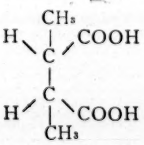
and



inactive.

In the formulæ for the inactive anhydride like groups correspond; according to Wislicenus this anhydride should therefore be the less stable. But the facts point the other way; hence Baeyer argues that correspondence of like groups does not involve instability, and suggests that the favored configurations of the acids have the following formulæ:





In both, methyl is opposite methyl, which explains the similarity in properties between these acids and the hexahydrophthalic acids in which the methylene chain answers to the methyl groups and must evidently have corresponding positions. If we ask why methyl should place itself near to methyl rather than to carboxyl, the answer is that the attraction of methyl for methyl (in ethane) is much greater than that of methyl for carboxyl (in acetic acid).

Thus, in order to explain why fumaric acid is more stable than maleïc acid, we must be prepared to maintain, if we accept Baeyer's hypothesis, that the attraction of H for COOH (in formic acid, two molecules) exceeds the attraction of H for H (in H_2, one molecule) together with the attraction of COOH for COOH (in oxalic acid, one molecule).

The Relative Position of Radicles connected with Two Carbon Atoms singly-linked—(Bethmann).

Having proved that the affinity-constant of a dibasic acid increases as the distance between the carboxyl groups diminishes, Bethmann showed that the introduction of a methyl group increased the constant of succinic acid, and explained this by the formulæ shown in Plate II., which represent how the attraction of methyl for carboxyl draws the carboxyls nearer together, thus raising the constant.

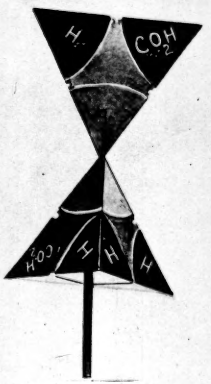
Here it will be seen that the arrangement of Wislicenus for succinic acid is altered. Carboxyl is not immediately over hydrogen, but immediately over a point half-way between the hydrogens which now attract the negative radicle equally.[1] The more strongly positive methyl, however, places itself directly opposite to the carboxyl. Introduction of another methyl group raises the affinity-constant again; that is to say, it causes a further approximation of the carboxyls, or, as Bethmann says, it causes the tetrahedron-axes to incline towards each other.[2]

Bethmann's results are not incompatible with Baeyer's formulæ for the dimethylsuccinic acids, since, as the models show, attraction between the methyl groups might also lead to approximation of the carboxyls.

A comparable case has been investigated in the laboratory of Wislicenus by Reisse, who examined the effect of the successive substitution of chlorine for hydrogen upon the decomposition of the sodium chlorlactates, which, on heating, yield sodium chloride, carbon dioxide and a chloraldehyde; *e. g.*,

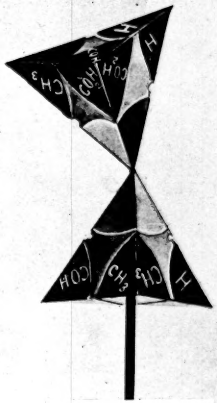
[1] W. P. Evans (Ztschr. phys. Chem. **7**, 337) also finds his results explicable only on the assumption that such "middle positions" represent the favored configuration in molecules analogous in structure to succinic acid.

[2] This conception would be necessary if the tetrahedra were regular. The tetrahedra $R-CH.CH_2.COOH$ and $R'-CH.H.COOH$ are, however, irregular (see note p. 42) and dissimilar; their axes probably already not in a line. Moreover, the inclination suggested represents more than is proved, viz., not only diminution of the distance between the carboxyl and probably between the methyl groups, but an increase of the distance between the hydrogen atoms. Still we may accept Bethmann's figures as a rough illustration of the facts.

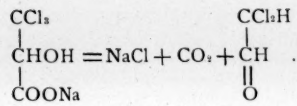


Succinic Acid
(Bethmann).

Methylsuccinic Acid
(Bethmann).



Dimethylsuccinic Acid
(Bethmann).



According to Bethmann's theory, the formulæ of the chlorlactates would be

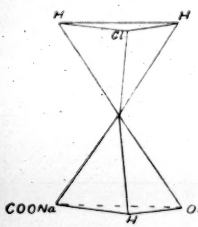


FIG. 25.

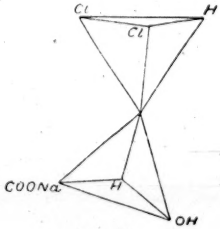


FIG. 26.

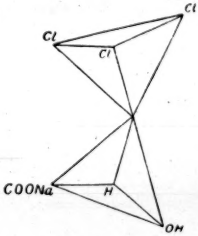
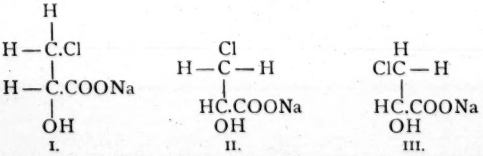


FIG. 27.

In the dichlorlactate the attraction of the two chlorine atoms for the two positive groups opposed to them causes bending and an approximation of these four radicles, but an approximation checked somewhat by the attraction of hydrogen for hydroxyl on the other side of the molecule. The substitution of chlorine for this hydrogen lessens the check, and in the trichlorlactate the approximation of sodium and chlorine is greatest. This should therefore be the readiest to decompose with formation of sodium chloride, and in fact it is so, the dichlorlactate also decomposing more readily than the mono-chlorlactate. Reisse's paper, however, was published a few days before the theory of Bethmann, and Reisse's explanation is different. "The three configurations of the trichlorlactate are all equally qualified to form sodium chloride, while only two configurations of the di- and only one (I) of the monochlorlactate (I, II, III) is capable of this decomposition":



Bethmann's hypothesis of the approximation of the carboxyl groups in the case of alkyl-succinic acids has been tested in

another way. If approximation of the carboxyls really takes place, this should show itself in their readiness to combine with exit of water, *i. e.* the introduction of methyl groups should facilitate the formation of anhydrides. Now Bischoff[1] finds that with regard to the ease with which they form anhydrides the methylsuccinic acids may be arranged in the following series: tetra-, tri-, di-, and mono-methylsuccinic acid. No explanation analogous to that given by Reisse for the decomposition of the chlorlactates is applicable here. Bethmann's hypothesis is; [and if we accept it we must reject the assumption, compatible with Reisse's view but incompatible with that of Bethmann] that the distance between two radicles connected by means of two carbon atoms varies between limits whose ratio is known: the minimum bearing to the maximum distance the ratio of the height of a regular tetrahedron to the length of its edge.

Further determinations of the affinity-constants of substituted succinic acids show, however, that the generalisations of Bethmann do not always hold good and "cut off all possibility of establishing laws generally valid" (Walden[2]). Ethyldimethyl-succinic acid *e. g.* has nearly the same constant as dioxysuccinic acid (mesotartaric acid), or the result of replacing three hydrogens by positive groups is nearly the same as that of replacing two hydrogens by negative groups.

The Space occupied by the Radicles in a Molecule—(Bischoff).

Bischoff, like Bethmann, had inferred that the carboxyl groups approach one another, and added that it may be supposed that the substitution of alkyl groups for hydrogen leaves too little room in the molecule for the hydroxyl groups, and hence the formation of the anhydrides. Many interesting applications of the theory of the crowding out of some atoms by others are given. Thus the following formulæ explain why monosodium carbonate, $NaHCO_3$, is stable while carbonic acid, H_2CO_3, cannot exist.

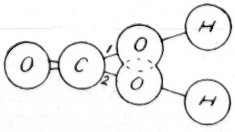


FIG. 28.

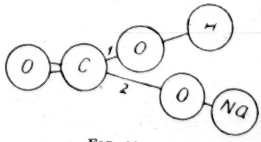


FIG. 29.

The affinity of sodium for oxygen is greater than that of hydrogen. Sodium will therefore bring oxygen nearer to itself and accordingly further from carbon; *i. e.*, the distance (2) in Fig. 29 is greater than the distance (1). Through this arrangement the

[1] Ber. d. chem. Ges. **23**, 620 and 3419. [2] Ztschr. phys. Chem. **8**, 433.

groups OH and ONa have room to oscillate without collisions. In Fig. 28 the distance 2 is as small as the distance 1 and collisions ensue, which cause splitting off of hydrogen and hydroxyl.

Further, the substitution of sodium for hydrogen in two hydroxyl groups may alter the angle between these groups.

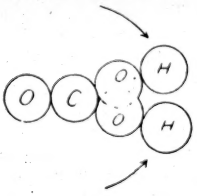


FIG. 30.

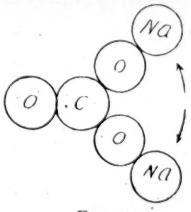


FIG. 31.

Both this and the increased distance of the oxygen atoms from the carbon atom have to be taken into account in considering the probable space-relations of the atoms. If, instead of sodium, alkyl groups be substituted for hydrogen in the hydroxyls, the results are similar and similarly explained. Hence it is that ethyl pyrocinchonate, $\begin{matrix}CH_3CCOOC_2H_5\\ \|\\ CH_3CCOOC_2H_5\end{matrix}$, can exist while the acid is known only as anhydride, $\begin{matrix}CH_3CCO\\ \|\\ CH_3CCO\end{matrix}\!\!>\!O$.

This answers the objection of Anschütz[1] that where there is no room for hydroxyl groups there can *a fortiori* be no room for ethoxyl groups. In fact, ethyl does not occupy the space indicated by the ordinary formulæ $\begin{matrix}CH_3CCOOC_2H_5\\ \|\\ CH_3CCOOC_2H_5\end{matrix}$, (the space which would be occupied by hydrogen $\begin{matrix}CH_3CCO\,OH\\ \|\\ CH_3CCOO\,H\end{matrix}$); but owing to its more strongly positive nature the ethyl group makes room for itself in a molecule from which the weaker hydrogen atom, though smaller, is excluded:

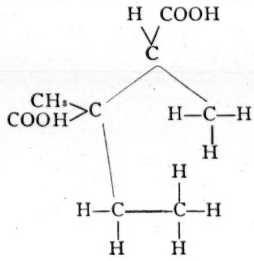
$$\begin{matrix}CH_3CCOO\,C_2H_5\\ \|\\ CH_3CCOO_{C_2H_5}\end{matrix}$$

[1] Ann. Chem. (Liebig) **259**, 145.

The idea of the crowding and collision of the groups in a molecule led Bischoff to a new conception, to his theory of "dynamical isomerism."

The Relative Motion of Indirectly Connected Radicals—(Bischoff).

If lack of space for the carboxyl groups of an acid cause exit of water, is this not because the hydroxyl groups come into collision, because the atoms of each come within the range of action of the atoms of the other? This leads to the question: What then will happen if the alkyl groups of the acid come into collision? Five carbon atoms singly-linked form almost a complete ring (see p. 574 *ante*); hence collisions may well occur between the radicles forming the ends of such a chain; *e. g.* between the alkyl groups of ethyl-dimethyl-succinic acid:



That the alkyl groups would be driven from the molecule was not probable; but further rotation might be hindered and each driven back along the path by which it came. The models show that this would lead to new cases of isomerism. Bischoff, however, could find no isomers not accounted for by Van't Hoff's theory, but was led to develop his own theory in order to explain the properties of the isomers he did find. He agrees with Baeyer that methyl does not repel methyl (I); and with Wislicenus that carboxyl repels carboxyl (II); further, he maintains that carboxyl repels methyl (III), urging as proof the non-existence of dimethyl-fumaric acid, $\begin{matrix}CH_3CCOOH\\ \|\\ COOHCCH_3\end{matrix}$, and the impossibility of forming it from pyrocinchonic acid, $\begin{matrix}CH_3CO\\ \|\\ CH_3CO\end{matrix}>O$; one methyl and one carboxyl group may, however, exist together (mesaconic acid $\begin{matrix}CH_3CCOOH\\ \|\\ COOHCH\end{matrix}$). It follows: *a*, that under the repellent action

of methyl groups a carboxyl may be forced to approach another carboxyl (see formulæ for tri- and tetramethyl-succinic acids); hence, (*a*) ready formation of anhydride; (*β*) rise of conductivity.

b. There is only one asymmetrical dimethyl-succinic acid, that in which carboxyl is removed from the methyl groups.

c. Ordinarily, carboxyl groups separate freely; succinic anhydride forms the acid with cold water:

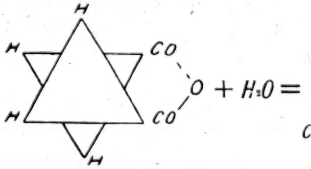


FIG. 32. FIG. 33.

But, when separation of the carboxyl groups would cause them to approach methyl, force must be used to effect it—heating with water under pressure.

As to III and *a* it may be said that mono- and dimethyl-succinic acids conduct better than succinic acid itself. Bischoff's formulæ (see figures) do not explain this; whereas Bethmann, assuming that methyl *attracts* carboxyl, was able to do so. If we express now Bischoff's conclusions in the phraseology of his theory, the result is not more convincing. He attributes, "with Van't Hoff," free rotation (see *ante*, p. 59) to ethane and its mono-derivatives, but supposes the position of rest for ethane to be

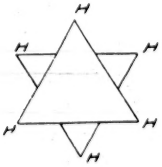


FIG. 34.

Van't Hoff has, however, long since given up (if he ever held[1]) the hypothesis of free rotation (*ante*, p. 60); and *free* rotation (*i. e.* rotation free from all resistance) is incompatible with rest at any temperature above absolute zero.

[1] Several authors say he did; Auwers, "Entwicklung," p. 8; Warder, *l. c.* Marsh encourages a similar view, "Chemistry in Space," p. 124. But the passage in "La chimie dans l'espace," p. 8, amounts only to saying that *if* rotation takes place, the different phases passed through do not represent different isomers.

"In other ethane-derivatives free rotation of the systems round the common axis is limited, and assuming collision of carboxyl with carboxyl and with alkyl groups, we may indicate by the dotted lines the path through which one of the carboxyl groups will oscillate." (See figures.) Here collision seems to be but another word for repulsion. The figures represent the favored configurations, "those in which the constituents least hinder one another's oscillations."

Here the formula for monomethyl-succinic acid which indicates collision between carboxyl and methyl, is in contradiction with Bischoff's statement (*l. c.* p. 1089) that the neighborhood of one methyl to one carboxyl group causes no collision. At present, however, the theories of Bischoff are apparently in a transition stage, and it is enough here to have indicated the new possibilities which they open up for stereochemistry.

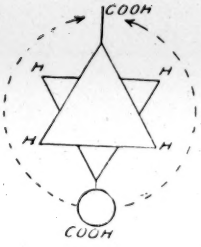
Conclusion.

We know by experiment that (1) crystalline compounds $C(R_1)_4$ belong to the regular system; (2) Compounds $CR_1R_2R_3R_4$ are optically active in solution; and (3) present a peculiar isomerism; (4) In substances $C(R_1)_2R_3R_4$ these peculiarities are lacking; (5) Substances $C_2R_1R_2R_3R_4$ are not optically active; but (6) present an isomerism different from that referred to in (3); Further, that (7) carbon rings are specially stable when they consist of five or six atoms; (8) Five carbon atoms form a ring of distinguished stability when combined with ten hydrogen atoms or their equivalent; (9) Six carbon atoms form such a ring with six hydrogen atoms or their equivalent.

Most of these statements of fact hold good for a considerable number of compounds; but, theory aside, each stands alone disconnected from all the others. Now all these general facts are connected together by the theories of Van't Hoff, and the first six of them by the theories of Le Bel.[1] Van't Hoff's theories being the more detailed require confirmation in detail. It is this confirmation which has in so many instances been brought by the investigation of particular cases of isomerism, although it has been seen also that in many cases more facts are needed before the connection between those already known can become apparent.

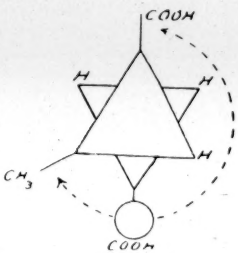
Our knowledge of the interaction of the radicles connected with carbon is in its first stage. Wislicenus assumed that this knowledge sufficed to enable us to represent with sufficient accuracy the configuration of ethane derivatives such as the dimethylsuccinic acids. Yet for these acids Baever, Bethmann and Bischoff have all suggested configurations differing from that of Wislicenus as well as from one another, so that there is now in the field almost as great a variety of these configurations as is compatible with the

[1] The connection between (5) and (6) depends on the proof that in ethylene derivatives the radicles connected with carbon are in one plane, for which see Le Bel, Bull. Soc. Chim. **37**, 300.



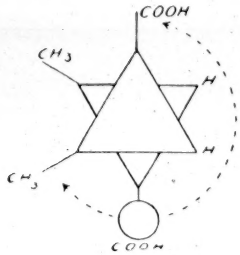
Succinnic.

FIG. 35.



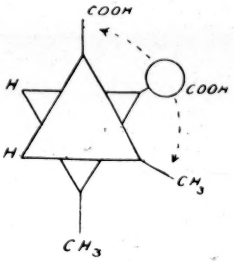
Monomethyl

FIG. 36.



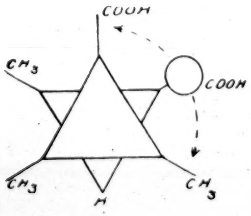
Para-dimethyl-

FIG. 37.



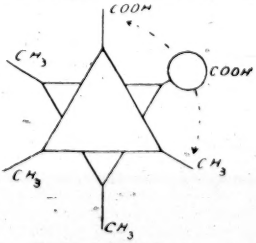
Anti-dimethyl-

FIG. 38.



Trimethyl-

FIG. 39.



Tetra-methyl-succinic acid.

FIG. 40.

theory of Van't Hoff (*ante*, p. 60) concerning ethane derivatives; yet not one configuration incompatible with it.[1] Thus that theory which at first startled chemists by the boldness with which it attempted so closely to define the positions of atoms, is now seen to be no less remarkable for the caution with which it avoided a definition closer than the facts warranted; advancing its conclusions at once up to the limits of just inference, the theory never pushed speculation beyond these limits. And recent stereochemical investigation may be described as an attempt to extend the limits within which Van't Hoff was confined, by determining the details of the interaction of indirectly connected radicles, especially in ethane derivatives, with a view to fixing the relative position of these radicles; this action may depend on a number of quantities, as (1) the affinity of the radicles for one another, (2) their affinity for carbon, (3) the distance between their centers of gravity, (4) the space occupied by them, (5) their relative motion. For no pair of radicles is any one of these quantities known absolutely, nor can we compare approximately one pair of radicles with another pair with respect to any one of these; usually we cannot say for which pair the quantity would be greater, and the uncertainty will continue as long as doubt remains concerning Wislicenus' "positive negative" hypothesis, or the proper substitute for it. These considerations render evident at once the extent and the importance of the work yet to be done; if stereochemistry is to advance, the problems indicated must advance side by side towards solution. And the continual attention which is now devoted to stereochemistry by German chemists, the fact that a stereochemical solution of each new structural mystery is ever held in mind, and the mass of work upon this subject constantly pouring from the laboratories of such investigators as Wislicenus, Baeyer and Bischoff, justify our confidence that the questions at present in dispute are on the way to settlement. Among the new problems then to be attacked will be the space-relations of elements other than carbon. Already the stereochemistry of nitrogen has formed the subject of many investigations, and this will be considered in a later review.

ARNOLD EILOART.

THE CHEMICAL ANALYSIS OF IRON. A Complete Account of all the best known methods for the Analysis of Iron, Steel, Pig Iron, Iron Ore, Limestone, Slag, Clay, Sand, Coal, Coke, and Furnace and Producer Gases. By ANDREW ALEXANDER BLAIR. Second Edition. Philadelphia: J. B. Lippincott & Co., 1891.

When Mr. Blair's book on the Chemical Analysis of Iron first appeared, chemists immediately recognised that they had acquired

[1] Even Bischoff's oscillation-configurations are not excluded, for we may derive them just as well from the heat-disturbance admitted by Van't Hoff as from the free rotation assumed by Bischoff.

a valuable and almost unique contribution to a special branch of analytical chemistry. Nothing had hitherto been written on this subject which approached Mr. Blair's book in completeness, accuracy, and usefulness. In the second edition, which has been called for by the prompt exhaustion of the first, Mr. Blair has still further increased the value of the work by careful revision and by the addition of much new matter. Many of the new processes described have been obtained from chemists of long experience in the laboratories of iron and steel works and represent the results of patient chemical experiment, and of much mechanical ingenuity, in perfecting methods for the rapid analysis of iron and steel—processes red-hot from the works, we might almost say. Mr. Blair mentions briefly—much too briefly, we think—the work of the American members of the International Steel Standard Committee, whereby our established practice and cherished theories regarding the determination of carbon in steel have been badly disturbed. This section of the book—the determination of carbon—is, from the standpoint of historical completeness, all that could be desired. But it still lacks the critical element which we think it needs. It will be found bewildering by the beginner who consults it to learn which are the most recent or most generally used processes. Mr. Blair has uniformly avoided a personal expression of opinion as to the accuracy of the processes he described with praiseworthy minuteness. There may be a wise prudence on his part in this restraint, but his readers would be often glad to know to which of the processes he gives the preference in his own practice. Book-makers are so often merely compilers that we do not ordinarily expect criticism and description to go hand-in-hand. But Mr. Blair could unite these processes with sure hand.

The tables of atomic weights and factors have been thoroughly revised for this edition, and the pages have been provided with a running title which greatly facilitates reference. We could have wished the author had in this edition rejected the use of symbols as abbreviations. If he were consistent in his practice in this regard, we might think he had entered on a crusade against the waste of time and space involved in writing chemical names in full. But when we see in five lines (to take an example at random) "Carbonate of Sodium," "Fe_2O_3," "H_2SO_4," "Titanate of Sodium," and "TiO_2," it looks as if the author were indifferent to the appearance of his (otherwise) handsome pages, and to the established usage of chemical writers. Shortcomings of this kind are the more to be regretted in a book which is largely used by "practical" chemists, who in their rush of work are only too apt to fall into careless forms of expression and writing.

We would like to repeat what was said in a notice of the first edition of the work, and which continued use of the book has fully justified, namely, that teachers of chemistry find this book of great value and convenience. It is impossible for a student to go astray in his work when he has this book in his hand.

THOMAS M. DROWN.

A HANDBOOK OF INDUSTRIAL ORGANIC CHEMISTRY. By SAMUEL P. SADTLER, Professor of Organic and Industrial Chemistry in the University of Pennsylvania. 8vo. J. P. Lippincott & Co., Philadelphia, 1891.

Professor Sadtler's book covers a field never before completely reviewed in any single work in English. The subjects treated are the following: petroleum, fats and oils, essential oils, sugar, starch, fermentation industries, milk industries, vegetable and animal textile fibres and their utilisation, leather, glue and gelatine, destructive distillation of wood and coal, artificial coloring matters, natural dye-colors, bleaching, dying and textile printing. Each subject is subdivided into five sections, viz.: materials, processes, products, analytical tests and methods, bibliography and statistics. With so wide a field to cover in a single volume of 500 pages, the treatment of each subject is necessarily brief, and many details which would have added to the interest of the work are unavoidably omitted. On the whole the book is a remarkable example of successful and satisfactory condensation, a result largely due to very systematic arrangement of the material.

A great deal of patient labor has been expended by the author in collecting statistics in regard to the various industries. These are of value in estimating the relative importance of different localities of production, and will prove a great convenience to teachers of industrial chemistry. The figures are well brought up to date, for the most part including the year 1890. The lists of books of reference are also full and valuable. Except in the case of analytical methods, references to periodical literature are not generally given. This is to be regretted, as many articles of great interest on the subjects treated have lately appeared, such as the papers on petroleum by Mendelejeff and Redwood in the Journal of the Society of Chemical Industry.

An excellent feature of the book is the full account given of American processes of manufacture. In this respect the work contains much that is not to be found elsewhere. Fuller information in regard to the particular sections of the country where the important industries are chiefly developed would have given increased interest to the processes described. A number of ingenious graphic outlines of the chief industries are given; these are very instructive, and excellent for purposes of review. Care has been taken to give credit to the authors in case of tables or illustrations taken from other works. The chief criticism which the reader will be disposed to make will be on the ground of too great brevity, for in examining so good a book it is impossible to resist the regret that there is not more of it. The chapter on artificial coloring matters is a very satisfactory brief outline of this complicated subject, and presents the most important facts in regard to the coal-tar colors in a way which will be welcome to English-reading students. The book closes with an appendix containing useful metric, thermometric and specific gravity tables.

S. B. N.

A System of Inorganic Chemistry. By William Ramsay, Ph. D., F. R. S., Professor of Chemistry in University College, London. London: J. & A. Churchill, 1891. xvi + 700 pp. 8vo.

The author has attempted in this book to bring into the subject of inorganic chemistry the same order that is characteristic of organic chemistry. He finds in the periodic law the basis of a rational classification of the elements and their compounds. On this subject he remarks: "Nearly twenty-five years have elapsed since the discovery by Newlands, Mendeléeff, and Meyer of the periodic arrangement of the elements; and, in spite of the obvious guide to a similar classification which it furnishes, no systematic text-book has been written in English with the periodic arrangement of the elements as a basis." Before proceeding farther it may not be out of place to point out that this statement needs modification. Richter's Inorganic Chemistry, of which we have an English translation, and the "Text-book of Inorganic Chemistry" by the writer of this notice, are both based upon the periodic law. To be sure, in neither one is the periodic arrangement followed pedantically; though, on the other hand, the deviations from the paths pointed out by the law are few—not greater in number in fact than those of which Professor Ramsay himself has been guilty, if to deviate at all be a crime. As to this he says: "The periodic arrangement has been departed from in two instances: the elements chromium, iron, manganese, cobalt, and nickel have been taken after those of the aluminium group; and the elements copper, silver, gold, and mercury have been grouped together and considered after the other elements. It appeared to me that the analogies of these elements would have been obscured, had the periodic arrangement been strictly adhered to." While arresting attention to an error of statement on the part of our author, it appears that the writer of this heartily agrees with him that the periodic law is the best foundation at present known for a rational treatment of the science of chemistry.

Among the reasons which, according to Professor Ramsay, have led to the prevailing unsatisfactory treatment of inorganic chemistry are:

1. "That the ancient and arbitrary line of demarcation between the non-metals and the metals has been adhered to;"

2. "That too great importance (from the standpoint of pure chemistry) has been assigned to the distinction between acid hydroxides and basic hydroxides (acids and bases), which has tended to obscure the fact that they belong essentially to the same class of compounds, viz., the hydroxides;" and

3. "That the chemistry of text-books has almost always been influenced by commercial considerations."

As regards the first two reasons it should be remarked that, while no doubt the author is right, on the other hand it is possible to err in the opposite direction, and not lay enough stress on the differ-

ences between the elements, and between their hydroxides, oxides, etc. It is certainly true that a sharp line cannot be drawn between the two classes of elements and between the two classes of hydroxides, etc., but it is also true that there are fundamental differences of some kind between these two classes, and that these differences are among the most important facts in the field of chemistry, and any system that does not emphasize them is not true to nature. The pointing out of analogies is not the only thing necessary; differences must also be pointed out. A satisfactory picture of the field can be given only by taking account of the lights and shadows. A map serves a very useful purpose, but it fails to give us much information of the highest value as regards the character of the country represented. An examination of the book under consideration shows that much has been sacrificed to systematic arrangement.

As regards the third reason above given, viz., the influence of commercial considerations, the writer fully agrees with Professor Ramsay. Descriptions of manufacturing processes still play too prominent a part in text-books of chemical science, and students unquestionably get wrong impressions concerning the relations of these processes to the science. It is a step in the right direction to relegate these descriptions to an appendix. By the above it should not be understood that there is any objection to teaching the students something about the manufacturing processes. On the contrary, it is well to call their attention to important applications of chemical truths. But such treatment as will serve unduly to magnify the importance of these processes or to create the too common impression that the chief object of the science is to furnish such methods, is to be avoided.

Having thus briefly considered the method of the book let us turn to the execution. Here there can be no hesitation in saying that the author has most conscientiously carried out the plan adopted by him, and he has therefore produced a book of value, though, like all other books, it has its limitations. First as to the plan. The subject is divided into nine parts. Part I treats of matters introductory and historical; Part II of the elements, arranged in six groups; Part III of the halides; Part IV of the oxides, sulphides, selenides and tellurides; Part V of the borides, carbides and silicides; Part VI of the nitrides, phosphides, arsenides, antimonides; Part VII of alloys and hydrides; Part VIII of spectrum analysis, the atomic and molecular weights of elements, and the molecular weights of compounds, the periodic arrangement of the elements; Part IX of processes of manufacture, commercial preparation of the elements, utilisation of sulphur dioxide.

This plan is well adapted to a work of reference, and it may be predicted that whatever success the book may meet with will be due to the fact that it contains brief and accurate descriptions of a

large number of substances arranged in an orderly way. In this respect it is superior to any existing book of its size. Many compounds that find no place except in the large dictionaries or the largest text-books are here mentioned and assigned their proper place in the system. While helping the student to get information in regard to individual compounds, long continued use of a book of this kind for reference would serve to impress upon his mind the general relationships between the compounds. For such use the book can be cordially recommended.

But from what has been said it will be concluded that the book does not appear to be as well adapted to the uses of the student who is trying to inform himself regarding the fundamental principles of chemistry. From a pedagogic point of view the treatment of all the elements at the beginning cannot be commended. The reactions made use of in the preparation of these elements are quite unintelligible to the beginner, and the plan necessitates the introduction of too much that is unintelligible before a single chemical reaction is discussed so fully as to give the student a clear impression regarding it.

Again, the author is unusually conservative in the matter of the conceptions that enter so largely into what is called modern chemistry. The views regarding the constitution of the compounds of carbon held by most chemists make the orderly treatment of organic chemistry possible. The phenomena of substitution and valency, as is well known, are at the basis of the prevailing views. To some it seems that in dealing with inorganic compounds we shall probably be obliged to follow the paths already followed by those who have developed the subject of organic chemistry. Careful study of the phenomena of substitution and valency has, it can be fairly claimed, been of great service in the study of the relations between inorganic compounds. Yet to these phenomena Professor Ramsay gives very little attention. When the subject of valency is first referred to, he says: "For these reasons it is concluded that the general formula of the halides of this group (calcium group) of elements is MX_2, where M stands for metal and X for halogen; that of the members of the lithium group is MX. Lithium and its congeners are termed *monad* or *monovalent* elements in these compounds; beryllium, magnesium and elements of their groups are termed *dyad* or *divalent* in their compounds. But it has been amply shown that *valency*, as the property of acting as a monad, a dyad, a triad element is termed, is not a constant quality of any element: nor in such compounds as KI_3, or in the double halides mentioned, can we tell how the atoms are held together, whether the metal attracts halogen, or halogen attracts halogen, or both attracts both. We are at present without any satisfactory theory to account for such compounds, and must, in the meantime, simply accept the fact of their existence."

Attaching as little importance to the phenomena of valency as the author does, he cannot attach much more to the subject of chemical constitution in the usual sense, and it is therefore not surprising that in general he takes but little advantage of prevailing views on constitution for the purpose of bringing out analogies. Though it is surprising that in some cases of complicated compounds concerning the constitution of which we have practically no knowledge based upon experimental study, as, for example, sphene (p. 313) and the analogous compounds, ultramarine, sodalite, nosean (p. 316)—that in such cases he should give constitutional formulas with some degree of confidence. Again, it is not surprising that the author makes free use of the conception of "double compounds." In this class, indeed, he prefers to put the hydroxides and the hydrosulphides. It may be that, as far as our knowledge of calcium hydroxide as an individual is concerned, the formula $CaO.H_2O$ is as good as $Ca(OH)_2$, but surely convictions reached by the study of chemical compounds in general are worth something. The hydroxide theory has been weighed these last thirty years and it has not been found wanting. That which we regard as evidence of the constitution of the alcohols is also evidence that the metallic hydroxides have the same constitution. To accept the hydroxide view is to simplify the study of a large number of the most important chemical reactions. What has been said concerning the hydroxides is applicable to other classes of compounds. Professor Ramsay would have improved his book by taking fuller advantage of the prevailing conceptions concerning the constitution of chemical compounds.

While the book seems open to some adverse criticism, it is only fair to say that it has many valuable features to recommend it, and especially those students who have got over the first difficulties in the study of chemistry will find it helpful. I. R.

NOTES.

Free Hydroxylamine.

The attempts of Lossen[1] to obtain hydroxylamine in the free state seem to have met with little success. His endeavor to separate the base by distillation after having decomposed the hydrochlorate by means of a strong alkali solution, generally

[1] Ztschr. Chem. [2] **1**, 151; Ann. Chem. (Liebig) Suppl. **6**, 229; **160**, 242.

resulted in its decomposition with evolution of ammonia. Victor Meyer, having recently questioned[1] the accuracy of the usual statements with regard to the great instability of free hydroxylamine, C. A. Lobry de Bruyn has now published a preliminary paper,[2] giving the results of his researches in this field up to the present time.

Since the introduction of the amido group in the place of hydrogen generally results in the formation of a compound with higher melting- and boiling-point than the original compound possesses, it would seem probable, this author thinks, that a compound which bears to water the relation of an amido derivative would be a solid at ordinary temperatures. This reasoning is justified by the facts discovered.

Believing that the presence of water had been fatal to the success of Lossen's experiments, Lobry de Bruyn has employed absolute methyl alcohol as solvent, having found that the hydrochlorate is more soluble in this reagent than in its homologue, absolute ethyl alcohol. In this medium the salt was treated with sodium methylate, after which the mixture was freed by filtration from the sodium chloride formed. The liquid was now found to contain free hydroxylamine, and on exposure to the air gave evidence of but slight decomposition.

On distilling the mixture it was found that some hydroxylamine passed over with the alcohol, but that the amount of loss from this source was lessened by decreasing the pressure inside the distilling apparatus. Finally, under a pressure of but 60 mm., nearly all the alcohol was removed and, by fractioning the residue, a product was obtained which solidified in the receiver, and which, after being several times pressed between layers of filter-paper and dried, was found to consist of hydroxylamine 99.4 per cent. pure. Still purer specimens have since been obtained.

Pure hydroxylamine is a white, odorless solid, crystallising in needles which melt at 33°. Heated rapidly it explodes, the flame produced being of an intense yellow color. It is only slightly soluble in chloroform, benzene, ether, ethyl acetate or carbon bisulphide. It is readily soluble in water, being in fact so deliquescent that the crystals rapidly become liquid when exposed to the air; in this condition it slowly evaporates. Strong aqueous solutions of hydroxylamine, when free from salts and protected from the air, are permanent; a solution containing 60 per cent. of the base was found to be unchanged after having stood for several months. Dilute solutions suffer slow decomposition when boiled.

When protected from the action of alkalies hydroxylamine is stable: care has to be taken, however, that the glass vessels used for its preparation and preservation shall not bring about decomposition, so sensitive is it to the action of even minute quantities of alkali.

[1] Ann. Chem. (Liebig) **264**, 126. [2] Recueil trav. chim. **10**, 100.

Bromine and iodine attack the base vigorously, giving rise to the formation of nitrous oxide—

$$2NH_2OH + 4Br = N_2O + 4HBr + H_2O.$$

The difference in the behavior of ammonia and of hydroxylamine towards the halogens is worthy of notice.

A peculiar property of hydroxylamine when in the liquid state is its power to dissolve salts as, for example, sodium chloride; on evaporation the salt is thrown down in crystalline form. Further work in this field is now being prosecuted.

Since the publication of Lobry de Bruyn's paper a short article has appeared,[1] in which the experiments of L. Crismer in the same direction are described. On heating the compound of zinc chloride and hydroxylamine, $ZnCl_2.(NH_2.OH)_2$,[2] Crismer found that the base distilled off and could be condensed in a proper receiver. As, however, the presence of free chloride of zinc is disadvantageous, the two following methods were devised to meet this difficulty:

(*a*) The salt was decomposed by heating with anhydrous aniline under a pressure of but 20 mm., a compound of zinc chloride and aniline being produced. The hydroxylamine was condensed in the form of crystals.

(*b*) The salt was placed in a flask with absolute ether and decomposed by a current of perfectly dry ammonia. The free hydroxylamine goes into solution in the ether; distillation in a vacuum serves to remove the ether and to leave the base in a pure condition.

W. W. R.

The Preparation of Hydrazoic Acid.

E. Noelting and E. Grandmougin[3] have devised for the preparation of hydrazoic acid a method which does away with much of the difficulty inseparable from that of Curtius. Noting the fact that the introduction of nitro groups to replace hydrogen atoms in chlor-benzene renders that compound much more sensitive to the action of reagents, these investigators made use of dinitro-aniline, instead of aniline, as a starting-point in their work. Converting this into the corresponding diazo-compound, this into the perbromide, and then decomposing the latter by means of ammonia, they obtained dinitro-phenyl hydrazoate. By the action of alcoholic potash the ether is decomposed with the formation of the potassium salts of hydrazoic acid and of dinitro-phenol. The products of the several reactions may be thus represented:

$$(NO_2)_2.C_6H_3.NH_2 \rightarrow (NO_2)_2.C_6H_3.N_2.NO_3 \rightarrow (NO_2)_2.C_6H_3.NBr—NBr_2$$

$$\rightarrow (NO_2)_2C_6H_3.N\begin{matrix}N\\ \|\\ N\end{matrix} \rightarrow KN\begin{matrix}N\\ \|\\ N\end{matrix}.$$

The mixture of the solutions of the salts is acidified and heated, when hydrazoic acid distils off. The investigation will be con-

[1] Bull. Soc. chim. (Paris), [3] **6**, 793. [2] Ibid. [3] **3**, 115.
[3] Ber. d. chem. Ges. **24**, 2546.

tinued in order to study the behavior of other di-substitution-products of aniline under similar conditions. W. W. R.

The Vapor-density of Ammonium Chloride.

The literature of abnormal vapor-densities has received another addition in a paper by O. Neuberg,[1] who, by the use of an apparatus devised by Lunge and himself, has been enabled to determine the vapor-density of ammonium chloride under greatly diminished pressure.

The apparatus used[2] is a modification of that of Victor Meyer, the novelty consisting in the use of Lunge's "Volumeter" for the collection and measurement of the air displaced from the vaporising-tube through the volatilisation of the substance experimented with. The graduated tube in which the air is to be measured is connected with a reservoir of mercury, as is also a closed tube containing as much air as at 0° and 760 mm. pressure will occupy a volume of exactly 100 cc. when the level of the mercury in it is at the zero-mark. The two latter are so arranged that they can be raised or lowered as the experimenter may desire. By means of a three-way cock the air-measurement tube can be at will connected with the vaporising-apparatus, or, on the other hand, with the outside air.

By successively lowering the reservoir when the vaporising-tube and the measuring-tube are in communication, and raising it again when the latter is open to the air and communication with the vaporising-tube has been cut off, the pressure of air in the apparatus can, if it be desired, be reduced to as little as 20 mm.

The pressure having been reduced to the proper point, and connection between the vaporising-tube and the measuring-tube having been established, the volatilisation of the substance is brought about, the tension being constantly maintained by lowering the reservoir as the level of the mercury in the measuring-tube falls. After equilibrium has been reached, communication with the vaporising-tube is cut off, and the 100-cc. tube and the reservoir are raised until the level of the mercury in all three vessels is the same. Under the conditions the gas in the 100-cc. tube will occupy more than 100 cc. The amount of this expansion being noted, the volume of the air in the measuring-tube is read, and, being expanded in exactly the same proportion as the gas in the 100-cc. tube, its volume at 0° and 760 mm. pressure may readily be deduced. The vaporising-tube can of course be filled with ammonia, hydrochloric acid gas, nitrogen, carbon dioxide, etc., instead of air, if it be so desired.

Using a pressure of 25 mm., Neuberg found the vapor-density of ammonium chloride in a tube filled with air to be (*a*) 1.13 and (*b*) 1.2; at a pressure of 46 mm. and in hydrochloric acid gas, (*c*) 1.5; and under a pressure of 60 mm. and in an atmosphere of

[1] Ber. d. chem. Ges. **24**, 2543. [2] Ibid. **24**, 729.

ammonia, (*d*) 1.68 and (*e*) 1.71. The theoretical vapor-density of the salt is 1.85, and that of a mixture of the gases ammonia and hydrochloric acid, of course, 0.925.

For sulphur vapor a density corresponding to the formula S_8 was obtained. W. W. R.

Iron-carbon-oxide.

Under the above title, Mond and Quincke—following up the discovery, by themselves and Langer, of nickel tetracarbonyl[1]—announced some months ago[2] the preparation of what they supposed to be the corresponding compound of iron. Ferrous oxalate, reduced in a current of hydrogen at 400°, was subjected to the action of carbon monoxide at a temperature of 80°; under these conditions an exceedingly small quantity of a volatile compound of iron and carbon monoxide was formed, and this on analysis gave figures corresponding to the formula $Fe(CO)_4$. In a recent paper[3] Mond and Langer report later and more successful efforts to obtain the compound in quantity and in pure condition. The details of the method of preparation cannot be given here.

Iron carbonyl is a liquid of sp. gr. 1.466, capable of distillation at the atmospheric pressure. It boils at 102.8 and solidifies below —21°. It is soluble in alcohol, ether, chloroform, and mineral oils. The vapor is decomposed at a temperature of 180° into iron and carbon monoxide. Analyses of the liquid and determinations of the density of its vapor both point to the formula $Fe(CO)_5$ as representing the composition of the substance. The authors therefore propose the name "ferro-pentacarbonyl" for the compound, and are of the opinion that the analyses recorded in the former paper were made with an impure material.

Ferro-pentacarbonyl is not affected by dilute acids at ordinary temperatures; concentrated nitric acid, chlorine-water and bromine-water, however, convert it into the corresponding ferric compounds. Alcoholic solutions of the alkalies dissolve ferro-pentacarbonyl without escape of gas. With mercuric chloride a compound is produced containing mercury, iron, chlorine and carbon monoxide; analyses did not, however, give figures from which a definite formula could be deduced.

When exposed to the light, ferro-pentacarbonyl decomposes with the evolution of carbon monoxide and the formation of yellow, tabular crystals resembling flakes of gold. Analyses of these seem to indicate a composition to be represented by the formula $Fe_2(CO)_7$. It should be said that the authors were unable to make molecular-weight determinations by either the vapor-density or the freezing-point method. The behavior of re-agents toward this latter compound is for the most part the same as towards ferro-pentacarbonyl. W. W. R.

[1] J. Chem. Soc. **57**, 749; Abstract, This Journal **13**, 70.
[2] J. Chem. Soc. **59**, 604. [3] Ibid. **59**, 1090.